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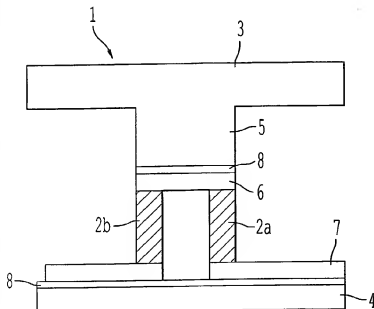
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- (54) Title: **THIN FILM THERMOELECTRIC DEVICES FOR POWER CONVERSION AND COOLING**

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(54) Title: **THIN FILM THERMOELECTRIC DEVICES FOR POWER CONVERSION AND COOLING**



(57) Abstract: A thermoelectric device having at least one thermoelectric unit including at least one thermoelectric pair of n-type and p-type thermoelements, a first header coupled to one side of the thermoelectric pair, and a second header coupled to a second side of the thermoelectric pair. The thermoelectric pair has a terminal conduction channel area smaller than an area of the first header or the second header such that the terminal conduction area is a fraction of the area of the first header or the second header.

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**TITLE OF THE INVENTION**

THIN FILM THERMOELECTRIC DEVICES FOR POWER CONVERSION AND COOLING

**5 Statement Regarding Federally Sponsored Research**

The U.S. Government, by the following contracts, may have a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms, as provided for by the terms in High-Performance Thin-film Thermoelectric Devices for Cooling and Power Generation, DARPA/ONR  
10 Contract No. N00014-97-C-0211, Thin-film Thermoelectric Palm Power Technologies, DARPA/ARO Contract No. DAAD19-01-C-0070, and Meta-Material Structures for Super-Radiant Structures, DARPA/AFOSR Contract No. F49620-01-C-0038.

**Cross- Reference to Related Documents**

15 This application is related to U.S. Provisional Application No. 60/372,139 entitled "Thermoelectric device technology utilizing double-sided Peltier junctions" filed on April 15, 2002, the entire contents of which is incorporated herein by reference. This application is related to U.S. Pat No 6,300,150 entitled "Thin-film thermoelectric device and fabrication method of same" issued October 9, 2001, the entire contents of  
20 which is incorporated herein by reference. This application is related to U.S. Pat No 6,071,351 entitled "Low temperature chemical vapor depositor and etching apparatus and method" issued June 6, 2002, the entire contents of which is incorporated herein by reference. This application is related to U.S. Pat No 6,505,468 entitled "Cascade cryogenic thermoelectric cooler for cryogenic and room temperature applications"  
25 issued January 14, 2003, the entire contents of which is incorporated herein by reference. This application is also related to U.S. Provisional Application No. 60/253,743 entitled "Spontaneous emission enhanced heat transport method and structures for cooling, sensing, and power generation", filed November 29, 2000, the entire contents of which is incorporated herein by reference, and subsequently filed as  
30 PCT Application No. PCT/US01/44517 filed November 29, 2001. This application is related to U.S. Provisional Application No. 60/428,753, "Three-Thermal-Terminal ( $T^3$ )

Trans-Thermoelectric Device”, filed November 25, 2002, the entire contents of which is incorporated herein by reference.

## DISCUSSION OF THE BACKGROUND

### 5 Field of the Invention

This invention relates to thermoelectric devices for power conversion and cooling which utilize thin film thermoelectric materials.

### Background of the Invention

10 A thermoelectric device can produce electrical energy when a heat flux flows through opposite conductivity types of a thermoelectric material. Furthermore, a thermoelectric device can cool an attached object when a current is flown in an appropriate direction through the thermoelectric material. In a thermoelectric generator, for example, a Seebeck voltage generated across a thermoelectric device can be used to  
15 drive a current in a connected load circuit. Indeed, thermoelectric generators can generate power from a variety of heat sources. For example, a thermoelectric power device can be connected to a wall of a combustion chamber and therefore generate power from the heat flux flowing from the combustion wall. In this example, a fuel is burnt to produce the heat flux for thermoelectric power generation; however, other heat  
20 sources applicable for thermoelectric generators include solar-heated sources, radioisotope-heated sources, and nuclear reactor waste heat sources. Thermoelectric generators typically include external electronic circuitry such as a DC-DC conversion circuits or DC-AC converters for receiving power from the thermoelectric elements at a low voltage and for delivering power at higher voltages.

25 In conventional thermoelectric devices, the efficiency of thermoelectric conversion is at about 6 to 8%. Accordingly, there is a drawback that thermoelectric conversion efficiency is low as compared with the other direct energy conversion systems such as for example a fuel cell device. If thermoelectric devices had higher conversion efficiencies, then thermoelectric power conversion devices could be  
30 effectively employed even in automobiles to increase the total fuel efficiency of the automobile by converting waste heat spent from the combustion process into electrical power.

Low efficiencies have also limited the application of thermoelectric devices in cooling and refrigeration applications. Chen *et al.* in U.S. Pat. No. 5,713,208, the entire

contents of which are incorporated by reference, describe a thermoelectric cooling apparatus which includes a plurality of thermoelectric coolers each having a hot side connected to a heat sink and a cold side coupled to an object to be cooled. While Chen *et al.* describe that thermoelectric coolers may be any suitable thermoelectric coolers such as those supplied by Melcor under catalog number CP 2-127-06L, the efficiency of these coolers, like those of the afore-mentioned power conversion thermoelectric devices, are limited.

The dimensionless thermoelectric figure of merit (ZT) is a measure of the effectiveness of the material for both cooling and power conversion applications. The Seebeck coefficient (S) is a measure of how readily electrons (or holes) convert thermal to electrical energy as the electrons move across a temperature gradient. At a given temperature, the thermoelectric figure of merit ZT for a given material is maximized at an optimum doping level. In most materials, the thermoelectric figure of merit ZT is maximized at doping levels of approximately  $10^{19} \text{ cm}^{-3}$ . Currently, the best non-superlattice thermoelectric materials have a maximum ZT of approximately 1. Today, bulk thermoelectric materials based on p-Bi<sub>x</sub>Sb<sub>2-x</sub>Te<sub>3</sub> and n-Bi<sub>2</sub>Te<sub>3-x</sub>Se<sub>x</sub> do not have a sufficient figure-of-merit (ZT) to allow economical application in many power conversion situations.

In contrast to bulk materials, the thermal properties of superlattice structures can be improved over that of the thermal properties of bulk materials. Superlattice structures in thermoelectric materials have been investigated as structures whose engineered properties can lead to better semiconductor and thermoelectric properties. The fabrication of a superlattice by molecular beam epitaxy (MBE), or other known epitaxial growth techniques, is generally known. The choice of materials and the relative amounts of the materials which make up the superlattice are factors in determining the characteristics of the superlattice. For use as a thermoelectric material, it is desirable to choose the materials, and their relative amounts, so that the thermoelectric figure of merit (ZT) and Seebeck coefficient (S) are maximized. Thus, superlattice materials are expected to have higher ZT values than bulk-materials. Despite the higher ZT of superlattice thin-film materials, thin film thermoelectric devices are presently limited by thermal mismatch and temperature gradient issues and also are practically limited by the high cost of thin-film superlattice materials.

#### SUMMARY OF THE INVENTION

One object of the present invention is to provide a thermoelectric device structure utilizing high ZT thermoelectric materials.

Another object of the present invention is to utilize a thermoelectric device structure in which the thermoelectric properties of the device are not contravened by  
5 inadvertent heat flux around the active thermoelectric elements in the device.

A further object of the present invention is to provide a thermoelectric device structure for cooling power-dissipating devices.

Still another object of the present invention is to provide a thermoelectric device which can convert power from a wide variety of moderate to high temperature heat  
10 sources, including but not limited to fuel sources.

Accordingly, one object of the present invention is to provide a multi-stage thermoelectric device for power conversion from heat sources at temperatures of 600 to 850K.

Still another object of the present invention is to provide a thermoelectric device  
15 which can be converted from a power conversion device to a heat pump device should coolant to a heat sink of the thermoelectric device be interrupted.

Yet another object of the present invention is to provide a thermoelectric device which utilizes both bulk thermoelectrics and superlattice thermoelectric films to exploit for each respective thermoelectric material those thermoelectric properties in operational  
20 temperature ranges most suitable for each.

Accordingly, one object of the present invention is to provide a thermoelectric device in which there is a high internal heat-flux within an individual thermoelectric stage and a low external heat-flux across the entirety of the thermoelectric device.

Various of these and other objects of the present invention are accomplished in  
25 several embodiments of the present invention.

One exemplary embodiment includes a novel thermoelectric device having at least one thermoelectric unit including a thermoelectric pair of n-type and p-type thermoelements, a first header coupled to one side of the thermoelectric pair, a second header coupled to a second side of the thermoelectric pair, and a thermal impedance  
30 increasing device disposed between the thermoelectric pair and one of the first and second headers.

## BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the present invention and many attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

5        Figure 1A is a schematic of one embodiment of a thermoelectric device according to the present invention;

Figure 1B is a schematic of a thermoelectric device according to the present invention operating in a High Active Flux- Low Input-Output Flux mode;

10        Figure 2 is a schematic of a multi-stage thermoelectric device according to the present invention;

Figure 3 is a graph depicting variations of ZT with temperature for various material systems useful in the present invention;

Figure 4 is a graph depicting state-of-the-art ZT vs carrier concentration for p and n-type Bi<sub>2</sub>Te<sub>3</sub>-based superlattice elements;

15        Figure 5 is a table of estimated design efficiencies for a three-stage thermoelectric device of the present invention;

Figure 6A is a schematic illustration depicting a thermoelectric device module of the present invention integrating a series of p-n couples on a single stage;

20        Figure 6B(1)-(3) depict tests on p-n couple devices of the present invention for open-circuit voltage (Voc), power (P), and power density (Pd in W/cm<sup>2</sup>);

Figure 6C is a table illustrating the inverted processing approach of the present invention;

Figure 7A is a schematic depicting the attachment of a pre-fabricated thermoelectric device of the present invention onto a semiconductor device chip;

25        Figure 7B is a schematic depicting the attachment of a thermoelectric device of the present invention onto a semiconductor device chip;

Figure 7C is a schematic depicting the sequential formation of a thermoelectric device on the present invention onto a semiconductor device chip.

30        Figure 8 is a schematic of a multi-stage thermoelectric device of the present invention employing resonant thermal energy transfer using Purcell-cavity enhancement effects and proximity-coupling of IR modes between various stages;

Figure 9 is a plot of apparent emission intensity as a function of the surface temperature of different engineered structures according to the present invention;

Figure 10 is a schematic arrangement of a three stage of thermoelectric device of the present invention with a split-header to provide thermal expansion relief;

Figure 11 is an electrical diagram showing a configuration for operating a thermoelectric device of the present invention in either a cooling mode or a heat pump mode;

Figure 12A is a schematic depicting a coupling structure for coupling a thermoelectric device to a semiconductor device chip;

Figure 12B is a schematic depicting another coupling structure for coupling a thermoelectric device to a semiconductor device chip;

Figure 13 is a schematic depicting another coupling structure for coupling a thermoelectric device to a semiconductor device chip;

Figure 14 is a schematic depicting a coupling structure including vias for electrical connections to the thermoelectric devices; and

Figure 15 is a schematic depicting a coupling structure including high thermal conductivity materials in a heat sink plate.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings, wherein like reference numerals designate identical, or corresponding parts throughout the several views, and more particularly to

Figure 1A thereof, Figure 1A depicts a schematic of one embodiment of a thermoelectric device according to the present invention. As shown in Figure 1A, a thermoelectric device 1 of the present invention includes a thermoelectric pair of n and p-type thermoelements 2a and 2b, respectively. The thermoelectric pair is connected thermally in parallel for heat conduction and electrically in series for electrical conduction. The thermoelectric pair of n and p-type thermoelements 2a and 2b are electrically adjoined together on the side coupled to an upper side header 3 by electrical connection 6, and are electrically connected separately on the side coupled to a lower side header 4 by electrical connection 7. As shown illustratively in Figure 1A, the thermoelectric pair of n and p-type thermoelements 2a and 2b can be coupled to the upper side header 3 by a heat pipe 5 made of high thermal conductivity materials such as Si, SiC, AlN, etc. In this example of the present invention, heat flowing in the thermoelectric device 1 is channeled in the heat pipe 5 into the thermoelectric pair of n and p-type thermoelements 2a and 2b.



In one embodiment of the present invention, due to the different thermoelectric properties of the n and p-type materials of the thermoelements **2a** and **2b**, electrons and holes in these materials diffuse at different rates across the respective n and p-type thermoelements, thereby creating a voltage difference across the pair of n and p-type thermoelements. In this embodiment, a cooling device (not shown) is coupled to the lower side header **4** to permit dissipation of heat. Otherwise, the upper side header **3**, the pair of n and p-type thermoelements **2a** and **2b**, and the lower side header **4** would all come to nearly equivalent temperatures. As a consequence, the electrons and holes in the n and p-type thermoelements **2a** and **2b** would stop diffusing to the lower-side header.

In another embodiment of the present invention, electron and hole current can be driven through the n and p-type thermoelements **2a** and **2b** by an applied voltage to thereby cool the upper side header **3**. Owing to electrical barriers existing between electrical connection **6** and the pair of n and p-type thermoelements **2a** and **2b**, the electron and hole current will preferentially transport those electrons and holes having a higher thermal energy, thereby cooling the upper side header **3**. A heat dissipation device (not shown) coupled to the lower side header **4** permits dissipation of heat from the device, else the lower side header **4** would come to a temperature such that heat, via diffusion of phonons, would flow back to the upper-side header **3** at a rate equal to the heat being carried from the upper-side header **3** by the electron and hole current, thereby eliminating the cooling.

The optional heat pipe **5** represents a mechanism to increase the thermal impedance (through the gaps) between the upper side header **3** and the lower side header **4** to a value significantly larger (by a factor of 100 or more) than the thermal impedance across the thermoelectric pair **2a** and **2b**. As shown in Figure 1A, the heat pipe **5** is elongated in a direction transverse to the thermoelectric device **1** (i.e., normal to the upper side header **3**). The heat pipe **5** has a cross-sectional area smaller than that of an area of the upper side header **3**. The heat pipe **5** of the present invention provides an offset, spacing apart the upper side header **3** from the lower side header **4**. The offset permits for example thin-film thermoelements to be used without thermal conduction from the upper side header **3** to the lower side header **4** shunting across the gap between therebetween, thereby forcing heat flux to flow through the thermoelements **2a** and **2b**. The offset in one embodiment of the present invention is at least 25  $\mu\text{m}$  and more preferably in the range of 250 to 500  $\mu\text{m}$ . As such, the offset produces a thermal

impedance across a gap, where thermoelectric elements do not exist, between the upper side header 3 and the lower side header 4 whose value is at much larger than the thermal impedance across the pair of thermoelements 2a and 2b. For example, a thermal impedance across an air gap is greater than the thermal impedances for the

5 thermoelements 2a and 2b, typically by a factor of 500 to 1000, for similar areas of air gap and thermoelectric materials. Thus, the offset allows this ratio to increase, using the high thermal conductivity of the offset relative to the air-gap. The thickness of the offset can be reduced as the pressure level in the gap is reduced i.e., with a high vacuum level, the thermal conductivity of the gap is reduced and so we need less of the offset

10 thickness. For many applications, the offset will be at least 10  $\mu\text{m}$ , and for other applications in a range of 100-500  $\mu\text{m}$ .

Regardless of the heat pipe, the thermoelectric devices of the present invention conduct a high active heat flux, while maintaining a much lower flux through the surfaces 1 and 4, through the pair of thermoelements which permits the present

15 invention to realize ultra-high specific power in the pair of n and p-type thermoelements 2a and 2b. Thus, the present invention operates with a high active flux through each of the thermoelements while having a low input/output flux across the entirety of the thermoelectric device. As described herein, this aspect of the present invention is referred as High Active Flux- Low Input-Output Flux (HAF-LIOF). This aspect is

20 illustrated pictorially in Figure 1B. In this aspect, the heat flux through the heat gatherer (e.g. an upper side header 3) and the heat spreader (e.g. an lower side header 4) is smaller than the heat flux through the n and p-type thermoelements 2a and 2b due to the reduced packing fraction of the thermoelements. A packing fraction of the thermoelements relative to the area of the heat spreader(s) permits the utilization of

25 thinner thermoelements, thereby reducing the fabrication costs that would be involved should for example thicker sections of high ZT materials be required to maintain the requisite  $\Delta T$  across the thermoelectric device.

The packing fraction of thermoelements (i.e., the fraction of area occupied by the pair of n and p-type thermoelements 2a and 2b relative to a unit area of for example the

30 upper-side header 3) in one embodiment of the present invention is less than 50%, less than 20%, and can be significantly lower, 0.5-1% for example. A unit area for the heat spreader is defined as that fraction of the total area of the heat spreader which principally conducts heat into one of the associated pairs of n and p-type

thermoelements attached to the heat spreader. For the single pair of n and p-type thermoelements shown in Figure 1B, the unit area would be the entire area of the upper side header 3. For instance, while the total heat flux into upper-side header 3 and out the lower-side header 4 can be on the order of 10 - 30 W/cm<sup>2</sup>, the heat flux through each thermoelectric pair 2a and 2b can be as much as a factor of 100 times higher.

The preferred packing fraction is a function of the heat flux available at the heat-source, the required  $\Delta T$  needed across the thermoelement to achieve the maximum efficiency, and the heat-flux that can be dissipated at the heat-sink. For example, if the required heat-flux through the device element is 2500 W/cm<sup>2</sup> to generate a requisite  $\Delta T$ , and the heat-flux that can be efficiently dissipated at the heat-sink is 25 W/cm<sup>2</sup>, then a packing fraction of 1% will be used (i.e.  $25/2500 \times 100\%$ ). However, if the heat-flux that can efficiently be dissipated at the sink is only 2.5 W/cm<sup>2</sup>, then a packing fraction needed would be 0.1% for the same heat-flux of 2500 W/cm<sup>2</sup> through each thermoelectric pair. A smaller packing fraction, however, can result in increased parasitic thermal transfer losses through any medium (such as air, Nitrogen, Helium) between the hot and cold-sides of the thermoelectric module.

Therefore, in thermoelectric devices of the present invention, besides using a heat pipe, other thermal impedance increasing devices can be employed. For example, a partial vacuum (i.e. ~1 Torr) as a low thermal impedance medium can be used in a module (e.g. the module 10 encapsulating the thermoelectric devices shown in Figure 6A) containing the thermoelectric devices. Alternatively, the module 10 can be filled with a low conductivity gas such as for example Ar.

The headers and heat pipes of the present invention have thermally conducting properties. Examples of suitable materials for the headers and heat pipes include for example AlN, SiC, and diamond. These materials have relatively high thermal conductivities (e.g. 5-20 W/cm-K) and offer the advantage of being electrically insulating. Alternatively, metallic or other semiconductor materials can be used for the headers and heat pipes of the present invention provided a suitable electrical insulating layer 8 is added to the surface of those materials. The thermal conductance through the electrical insulating layer preferably presents no substantial impediment to vertical heat flow through the pair of n and p-type thermoelements 2a and 2b.

For example, the headers of the present invention can be made from a Si substrate of a thermal conductivity of ~ 1.2 to 1.6 W/cm-K having a thin (i.e. ~10 nm to 1000 nm) SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> layer of a thermal conductivity of ~ 0.015 W/cm-K deposited

thereon. For example, the headers of the present invention can also be made from a Cu substrate of a thermal conductivity of  $\sim 4$  W/cm-K having a thin (i.e.  $\sim 100$  to  $1000$  nm)  $\text{SiO}_2$  or  $\text{Si}_3\text{N}_4$  layer of a thermal conductivity of  $\sim 0.015$  W/cm-K deposited thereon. If a SiC header or heat pipe is used that is electrically conducting (e.g. a doped SiC material), a similar insulating layer can be applied as well.

Since the thermoelements are low voltage, high current devices, the electrical connections are preferably highly conductive having a low resistance (preferably  $1/10^{\text{th}}$  or less than that of the Ohmic resistance of the thermoelements). A low conductance for the electrical connections will undermine the efficiency of the thermoelectric stage by resistive losses in current flow through the thermoelectric device.

Accordingly, in general, the present invention includes a thermoelectric device having a first header (e.g. the upper side header 3) coupled to a heat source, a pair of n-type and p-type thermoelements (e.g. the pair of n and p-type thermoelements 2a and 2b) coupled to the first header and configured to conduct heat from the first header, a second header (e.g. the lower side header 4) coupled to the pair of n-type and p-type thermoelements and configured to conduct heat from the thermoelectric pair, and a heat pipe coupled to the pair of n-type and p-type thermoelements (e.g. the heat pipe 5 connected to the thermoelectric pair 2a and 2b) and elongated in a transverse direction across the thermoelectric device to separate the first header from the second header.

In one embodiment of the present invention, the thermoelectric devices cool the first header (and thus can cool heat dissipating devices coupled thereto) by the flow of an electrical current through electrical connections 6 and 7 through the thermoelements 2a and 2b, thus transporting heat in the electrical carriers (i.e., the electrons and holes) and thereby cooling the first header. In another embodiment of the present invention, the thermoelectric devices generate electrical power by the development of a voltage on the electrical connections 6 and 7 as heat flows from the first header (coupled to a heat source) through the thermoelements 2a and 2b to the second header (coupled to a heat sink).

Further, the present invention is not limited to single stage and/or single pair thermoelement devices but can utilize multiple stages and/or multiple pairs of thermoelements in a single stage.

Figure 2 depicts a multi-stage embodiment of the present invention. Specifically, Figure 2 is an illustrative schematic of a multi-stage or multi-unit thermoelectric device of the present invention including three thermoelectric stages or

units. The device depicted in Figure 2 is shown by way of example in a configuration for thermoelectric power conversion and, for simplicity, is discussed below only in a context of power conversion. However, the features of the present invention depicted in Figure 2 and utilizing multiple stages and/or multiple pairs of thermoelements in a stage are, according to the present invention, applicable to thermoelectric cooling as well. Further, the number of stages and the number of thermoelectric pairs per stage in the present invention are not restricted to that illustrated in Figure 2.

As shown in Figure 2, an upper header 12 is coupled to a heat source 14 and includes at least one upper thermoelectric stage 16 coupled to the upper header 12. Of the thermoelectric stages 16, 17, and 18 depicted in Figure 2, at least one of the depicted thermoelectric stages is dimensioned such that area for thermal conduction in the thermoelectric stage through a pair of thermoelements 20a and 20b, herein referred to as the active thermal conduction channel area, is smaller than above-noted unit area of header 22 to which the pair of thermoelements 20a and 20b are coupled to. Such dimensioning as discussed with regard to Figure 1 establishes the HAF-LIOF aspect for the multi-stage thermoelectric device of Figure 2. As shown in Figure 2, the upper thermoelectric stage 16 is coupled to at least one lower thermoelectric stage, e.g. stage 17. The lower thermoelectric stage 17 like the upper thermoelectric stage 16 has an active thermal conduction channel area through the pair of thermoelements 20a and 20b that is smaller in area than the unit area of header 22. In the device depicted in Figure 2, heat is dissipated from the lower-most thermoelectric stage 18 by a heat sink 24 coupled thereto. Accordingly, heat pipes in the various stages also have at least one thermal conduction channel area that is smaller than the unit areas of the associated headers.

In the multi-stage thermoelectric device depicted in Figure 2, a high internal heat-flux exists within the individual thermoelectric stages (e.g.,  $\sim 1800 \text{ W/cm}^2$  for a  $\Delta T$  across each stage of 85K to as high as  $\sim 2300 \text{ W/cm}^2$  with a  $\Delta T$  across each stage of 107K). Meanwhile, a low external heat-flux exists across the entirety of the thermoelectric device (e.g., a range from 15 to 30  $\text{W/cm}^2$ ). In a multi-stage device, the packing fraction and hence the active flux through each stage can be different or similar to the active heat flux in other stages.

More specifically, the multi-stage thermoelectric device as illustrated in Figure 2 can include a high-temperature thermoelectric conversion stage (i.e. the upper thermoelectric stage 16), for example an N-SiGe/P-TAGS thermoelement pair (e.g., with a  $\sim 100 \mu\text{m}$  active region thickness). TAGS refers to a Tellurium, Antimony,

Germanium, and Silver (TAGS) alloy composition. TAGS compositions are in general denoted by  $(\text{AgSbTe}_2)_{1-x}(\text{GeTe})_x$ . The most optimal composition according to the present invention for x, the GeTe mole fraction, is ~0.80 to 0.85. As illustrated in Figure 2, the high-temperature thermoelectric conversion stage is coupled to a mid-  
5 temperature thermoelectric conversion stage (i.e. stage 17), for example an N-PbTe/P-TAGS thermoelement. As illustrated in Figure 2, the mid-temperature thermoelectric conversion stage is coupled to a lower temperature thermoelectric conversion stage (i.e. the thermoelectric stage 18), for example an n-type and p-type  $\text{Bi}_2\text{Te}_3$ -superlattice-thin-film thermoelement pair having a 5 to 10  $\mu\text{m}$  in thickness. As shown in Figure 2, the  
10 lower header 23 constitutes a split-header having slits formed partially (in the top side and correspondingly at certain locations on bottom side not shown) in a body of the lower header 23 to provide thermal expansion relief. In one embodiment of the present invention, the splits are preferably not located near the devices.

The three-stage thermoelectric device depicted in Figure 2 has a design  
15 efficiency in a range of 20% and electrical power density in excess of 5  $\text{W}/\text{cm}^2$ , and is capable of power conversion in a range of tens of mWatts to as high as 1 MWatt when coupled to a heat source at temperatures approaching 875K. Design efficiencies in excess of 20% and the capability to operate with hot-sides in the range of 675 to 875K permit flexibility and adaptability to real-world systems. With hot-sides in the range of  
20 675 to 875K, higher Carnot efficiencies are available then would be available for example in thermoelectric devices restricted to hot-sides of 375K to 575K. In turn, higher Carnot efficiency provides for higher system efficiencies which in turn facilitates load balancing by reducing the number of modules (i.e., the number of thermoelectric pairs) required to convert a given heat flux into electrical power.

25

### Materials Selection

While the concepts of the present invention are not restricted to any particular family of thermoelectric materials, the use of superlattice materials improves thermoelectric device efficiency of the multi-stage thermoelectric device of the present  
30 invention. Conventional bulk  $\text{Bi}_2\text{Te}_3$  thermoelectric devices offered by Hi-Z Inc. (San Diego, CA) exhibits a power density of 0.34  $\text{W}/\text{cm}^2$  at a  $\Delta T$  of 200K for a specific power of ~0.165  $\text{W}/\text{gm}$ . Yet, even unoptimized thin-film  $\text{Bi}_2\text{Te}_3$ -superlattice mini-module devices fabricated by the HAF-LIOF aspect of the present invention, even without the mid and high temperature thermoelectric power conversion stages discussed

above, have demonstrated a power density of  $0.7 \text{ W/cm}^2$ , with a  $\Delta T$  of  $77\text{K}$ , and a specific power of  $16.7 \text{ W/gm}$ . Specific power defined as the power produced per unit weight of the thermoelectric device. Both the specific power and the power density levels would increase with the addition of mid and high-temperature stages and further optimization of the low-temperature superlattice stage. Accordingly, the thermoelectric devices of the present invention can realize a specific power greater than  $1 \text{ W/gm}$  and a power density greater than  $0.5 \text{ W/cm}^2$ .

On the other hand, specific powers in a range of less than  $0.0001 \text{ W/gm}$ ,  $0.001 \text{ W/gm}$ , and  $0.01 \text{ W/gm}$ , are possible with the present invention and are applicable to applications such as for example bio-medical devices. In these applications, the HAF-LIOF devices could be used for heat gathering from low temperature sources in a range of  $30\text{--}40^\circ\text{C}$ . such as the human body for the powering of pacemakers or neuro-stimulators used to alleviate symptoms of Parkinson's disease or other neurological disorders.

Figure 3 is a graph depicting variations of  $ZT$  with temperature for various material systems useful in the present invention. Knowledge of the variation of  $ZT$  with temperature in suitable temperature-stable material systems, such as shown in Figure 3, permits appropriate materials selection for the above-described multi-stage design. The material selections should, according to the present invention, provide a material for each thermoelectric stage which is robust in the temperature range in which the thermoelectric stage is intended to operate. For example, devices in  $\text{PbTe/PbSe}$  and  $\text{Si/Ge}$  superlattice material systems would be useful for a temperature range of  $475\text{K}$ – $675\text{K}$  and  $675\text{K}$ – $875\text{K}$ , respectively, in the present invention.

The relevant properties, the lattice-mismatch and the bandgaps, of the  $\text{PbTe/PbSe}$  superlattice system are shown in Table 1.

**Table 1.**

Material	Lattice Constant (Å) at 300K	Velocity of Sound (cm/sec) at 300K	$E_g$ (eV) at 500K	$E_g$ (eV) at 600K	$E_g$ (eV) at 650K
PbTe	6.462	$1.26 \times 10^5$	0.4	0.445	0.468
PbSe	6.117	$1.42 \times 10^5$	0.38	0.431	0.457

Both materials  $\text{PbTe}$  and  $\text{PbSe}$  have similar thermal expansion coefficients; so that lattice mismatch at higher temperatures would be similar to that at  $300\text{K}$ . Also,  $kT$

at the temperatures of 500 to 650K is about 0.05 eV, comparable or larger to the bandgap difference between PbTe and PbSe. Thus, no barriers or quantum confinement effects will be present within the material, but a significant thermal conductivity reduction is expected in these superlattice materials.

- 5           Regarding the SiGe materials family, Si/Ge superlattice materials, according to the present invention, are attractive for high temperature applications (i.e., 650 to 850K). For example, Si/Ge superlattice materials deposited at ~1000K have shown a dramatic reduction in thermal conductivity and concomitantly an enhancement in ZT. Although Si/Ge superlattices may only offer a ZT of only ~0.8 at 300K, significantly below that of
- 10 a  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  superlattice or a  $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$  superlattice, the Si/Ge superlattices are likely to offer a much higher ZT at the higher temperatures employed in the upper thermoelectric stages depicted in Figure 2. Further, the SiGe superlattices will have higher ZT values than associated SiGe alloys of the same Ge concentration, leading to higher efficiencies. Indeed, development of high ZT thin films in the PbTe/PbSe and in
- 15 the SiGe material systems have been described by M. Lee *et al.* in Appl. Phys. Lett., 70, 2957 (1997) and R. Venkatasubramanian, Phys. Rev. B 61, p. 3091 (2000) and by R. Venkatasubramanian *et al.* in Proc. of 17<sup>th</sup> International Conference on Thermoelectrics, 191, (1998), the entire contents of which are incorporated herein by reference.

- In addition to superlattices, other quantum-confined structures and structures can
- 20 be utilized according to the present invention in which a strong thermal conductivity reduction is obtained while at the same time maintaining electrical conduction across the thermoelectric stages. For example, PbTe-based quantum-dot superlattices (QDSL) are suitable materials for the n and p-type thermoelements of the present invention. ZT values for these materials are achievable in a range of 1.5 to 2, in the temperature range
- 25 of 450K-550K.

- Furthermore, even ZnSb and skutterudites, (i.e., materials with a known  $\text{ZT} > 1$  over a temperature range suitable for power conversion) are also applicable in the present invention provided these materials are in thin substrate form (i.e. in a thickness of 100 to 200  $\mu\text{m}$ ) and are used in a temperature range of 500K to 900K. Thus, the
- 30 HAF-LIOF, high-power density, multi-stage power conversion device concept of the present invention is not limited to  $\text{Bi}_2\text{Te}_3$ -superlattice/PbTe/SiGe material combinations. Indeed, superlattices of Si/Ge, PbTe/PbSe, ZnSb/CdSb, InAs/InSb, CdTe/HgCdTe,  $\text{Ga}_{1-x}\text{In}_x\text{As}/\text{GaIn}_{1-y}\text{As}$  can be used in the high-temperature and mid-temperature



thermoelectric conversion stages, discussed above, thus providing a cascade thermoelectric device utilizing all superlattice materials.

For the lower temperature thermoelectric conversion stages of the present invention and for single stage cooling devices operating near room temperature, superlattice stages of  $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  can be used. Figure 4 is a graph depicting state-of-the-art ZT vs carrier concentration for p and n-type  $\text{Bi}_2\text{Te}_3$ -based superlattice elements. Figure 4 shows a  $\text{ZT} \sim 3.5$  in p-type superlattices and  $\sim 2.0$  in n-type. According to the present invention, by control and engineering of dopant carrier levels, the 300K figure-of-merit (ZT) achievable with p-type  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  and n-type  $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$  superlattice device elements is improved from previously known values of  $\sim 2.4$  and  $\sim 1.2$  to values greater than 3.5 and  $\sim 2$ , respectively. The carrier levels in the p-type materials as shown in Figure 4 are controlled by varying the organometallic Tellurium flow-rate during growth, for a fixed growth rate of the superlattices which in turn can be controlled by the flow-rate of the organometallic Bismuth for  $\text{Bi}_2\text{Te}_3$  and organometallic Sb for  $\text{Sb}_2\text{Te}_3$ . The carrier levels, for a constant growth rate, can also be controlled by control of growth temperature over a limited range. For the n-type materials, the doping levels as shown in Figure 4 can be controlled by the growth rates of  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$  layers in the superlattice as well as the growth temperatures. A value of peak ZT of  $\sim 2.9$  demonstrated in the present invention for a  $10\text{\AA}/50\text{\AA}$  p-type  $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  superlattice is one of the highest peak ZT values observed at 300K for the p-type  $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  superlattice material system. Such improvements in ZT permit improved power conversion efficiencies and cooling efficiencies for the thermoelectric devices of the present invention.

## 25 Device Performance

In the present invention, the advances in ZT for the p and n-type superlattice materials have been incorporated into fabricated p-n thermoelement couples. By flipping the fabricated p-n couples onto a split semi-infinite Cu-plate as opposed to flipping the fabricated p-n couples onto a header with a limited-thickness metallization, a more accurate measure of the thermoelectric properties of the fabricated p-n thermoelement couples is possible. For instance, each one of the p-n thermoelement couples potentially carries a high-current (i.e., several Amps of current) and is a low-voltage thermoelectric device. Parasitic lead resistances can therefore affect the measured device efficiencies. Properties of the p-n thermoelement couples have been

developed by fabrication and analysis of the p-n thermoelement couples on a split semi-infinite Cu-plate. In the fabricated thermoelectric devices, electrical contact resistances in the thermoelectric devices are minimized between the metallizations and the p-n thermoelement couples, providing adequate electrical interfacing.

5 In addition to managing electrical contact resistances, thermal interface resistances are reduced in the metal-to-dielectric interfaces of the present invention by deep-annealing of a metal into the dielectric bulk or by utilizing an AlN-diffused Al-Cu interface.

Further, high aspect-ratio thermoelectric devices (either with thicker superlattice  
10 films or smaller-area devices) are provided by appropriate patterning and etching of the p-n couples (e.g. the thermoelectric pair **2a** and **2b**). An aspect ratio of the element is defined as the ratio of thickness/area of element in units of  $\text{cm}^{-1}$ . Typical thickness of thermoelectric elements in the low-temperature stage can be about 5 to 20 microns, while the mid and high temperature stages can have thicknesses ranging from 50 to 250  
15 microns. The aspect ratio, hence the area of each element of the various stages, are based on the thermal conductivity of the materials (noting that the thermal conductivities of the p and n-type elements within a stage can be different and so their aspect ratios to allow same  $\Delta T$  across both p and n-type elements of each stage can be different) of the various stages and the required  $\Delta T$  for each stage for maximizing the  
20 efficiency of the overall set of stages. The  $\Delta T$  of each stage is inversely proportional to thermal conductivity of the material and directly proportional to the aspect ratio. Hence, according to the present invention, the total heat flux through each stage is same; thus the aspect ratio (and the associated packing fraction) in each stage is adjusted with this criterion to meet the design  $\Delta T$  for each stage.

25 Power conversion efficiencies achievable in for example the three-stage thermoelectric devices of the present invention are calculable based on known equations. The maximum efficiency is obtained when the load ratio  $r$ , defined as  $R_L/R_G$  with  $R_L$  being the load resistance and  $R_G$  being the thermoelectric device internal resistance, is optimized for average  $ZT$  over the entire temperature range,  $ZT_m$ . See, for  
30 example, H.J. Goldsmid, *Electronic Refrigeration*, Pion Limited, (1986).

Once  $r$  is known as per eqn. (1) shown below, the device efficiency  $\psi$  can be obtained by eqn. (2), shown below for a given  $\Delta T$ , temperature differential, and mean operating temperature  $T_m$ .

$$r = (1 + ZT_m)^{1/2} \quad \dots(1)$$

$$\psi = \Delta T / \{ [(r+1)/(r-1)] * T_m + \Delta T / 2 \} \quad \dots(2)$$

Power conversion efficiency estimates are shown in Table 2 of Figure 5, for a range of ZT values for each stage. The power conversion efficiency estimates are shown in a range from upper to midrange to lower projected values. The projections in Table 2 indicate that an efficiency in the range of 9.6% to 11.4% for a  $\Delta T$  of 150°C in the low-temperature Bi<sub>2</sub>Te<sub>3</sub>-SL-based stage can be realized for a ZT value of 2 to 2.5. An efficiency in the range of 4.3 to 4.7% for a  $\Delta T$  of 175 to 200°C in the n-PbTe/p-TAGS-based thin N-PbTe/P-TAGS thin-substrate mid-temperature stage can be realized for a ZT of ~0.75. An efficiency in the range of 3.4 to 3.7% for a  $\Delta T$  of 200°C N-SiGe/P-TAGS thin-substrate high-temperature stage can be realized for a constant ZT of ~0.75. Thus, according to the present invention, a thermoelectric efficiency of ~19.4% to 17.7% and a power density in excess of 5 W/cm<sup>2</sup> are obtainable in the three-stage thermoelectric power conversion devices of the present invention.

Indeed, Table 2 illustrates the performance of various stages of a three-stage thermoelectric device of the present invention as a function of ZT and the efficacy of thermal management at the heat-sink. The calculations in Table 2 are based on a module size of approximately ~33 cm<sup>2</sup>. For these examples, a heat flux of ~30 W/cm<sup>2</sup> is assumed to flow from the heat-source (i.e. the upper-most header) to the heat sink (i.e. the lower-most header), yielding a heat-flux dissipation range of ~24.7 to 22.7 W/cm<sup>2</sup> at the heat-sink. The power densities are calculated assuming a 5- $\mu$ m thick superlattice element in the low-temperature Bi<sub>2</sub>Te<sub>3</sub>-super lattice stage and assuming a 100- $\mu$ m thin-substrate for bulk thermoelements in the mid and high temperature stages. Table 2 indicates that higher ZT materials for both the mid-stage (460 -660K) and high-stage (670-890K) are advantageous.

For a given heat flow Q, in Watts, the aspect ratio determines the  $\Delta T$ . The efficiency is a function of  $\Delta T$  and ZT. The power generated P, in Watts, is a product of Q times efficiency. Thus, power density, Pd, is a function of both area, thickness, ZT and Q. Hence, according to the present invention, one approach to achieve power densities of greater than 20 W/cm<sup>2</sup> is to use thinner sections of thermoelement materials (e.g., preferably less than 300  $\mu$ m).

Calculations of thermal-to-electrical conversion efficiency, corrected for lead resistances, versus internal  $\Delta T$  across the flipped inverted p-n couple, and the ZT obtained from the efficiency equations indicate that about 85% of the external  $\Delta T$  (and consequently the heat flux) is applied across the device. The 15% loss is primarily due to the thermal interface resistance between the metallization and the AlN header. According to the present invention, the thermal interface resistance can be reduced in the metal-to-dielectric interface by deep-annealing of the metal into the dielectric bulk or by utilizing an AlN-diffused Al-Cu interface, as discussed above.

Calculated ZT values of the inverted couples utilized for demonstration of the power conversion concepts of the present invention were about a ZT value of 1.1 at 300K. The average ZT of the p-n couple of the present invention (e.g. the thermoelectric pair **2a** and **2b**) increases with temperature, consistent with the general trend of ZT shown in Figure 3.

One p-n couple of the present invention was tested up to a  $\Delta T$  of nearly 85K, corresponding to an active device heat flux within the thermolement of  $\sim 1800 \text{ W/cm}^2$ . For this tested p-n couple, the external heat flux was about  $28 \text{ W/cm}^2$  with a temperature rise of about 28K at the heat-sink. Application of improved thermal management practices to operate even this test device with a  $\Delta T$  of 150K, even with the present ZT of  $\sim 1.5$ , will permit an efficiency of  $\sim 8.6\%$  to be realized. Improvements in ZT values from 1.5 to  $\sim 2$  will realize in the present invention efficiencies of  $\sim 11\%$  for a  $\Delta T$  of 150K.

Accordingly, the present invention in one preferred embodiment includes a system for thermoelectric power conversion. The system includes a thermoelectric pair of n-type and p-type thermoelements, a first header coupled to one side of the thermoelectric pair, a second header coupled to a second side of the thermoelectric pair, a thermal impedance increasing device disposed between the thermoelectric pair and one of the first and second headers, and a heat sink coupled to the second header which dissipates heat at a rate which maintains a temperature of the second header below a temperature of the first header. Further, a coupling member can be used to couple the first header to a heat source. The heat source can be a combustion source, a radioactive source, a solar-heated source, and an electrical power device. The coupling member in one embodiment of the present invention can be a thermally conducting member having a thermal conductance of at least Al and extending between said first header and said

heat source. Alternatively, the coupling member can be a steam pipe or a combustion exhaust pipe transporting heat flux by a convective medium such as for example steam or combustion gases.

Figure 6A is a schematic illustration depicting a thermoelectric device module of the present invention integrating a series of p-n couples on a single stage. Tests on p-n couple devices for open-circuit voltage (Voc), power (P), and power density (Pd in W/cm<sup>2</sup>) are shown in Figure 6B. Tests on an integrated 16 p-n couple devices show expected open-circuit voltage (Voc), power (P), and power density (Pd in W/cm<sup>2</sup>). In particular, the open-circuit voltage has been observed to scale in the thermoelectric module to almost sixteen times that of a single-couple, for similar  $\Delta T$  to the individual p-n couple, further supporting the HAF-LIOF concept. The power levels of 38 mW per couple, for a 600  $\mu\text{m} \times 600 \mu\text{m}$  device and for a  $\Delta T$  of about 107K correspond to an electrical power density of as much as  $\sim 10.2 \text{ W/cm}^2$ . The power level scales to 166 mWatts per couple for the 16-couple module for a  $\Delta T$  of 77K.

Both p-type and n-type thin-film superlattice thermoelements of the present invention have been stable. Exposures to temperatures of  $\sim 450\text{K}$  and times of up to 60 hours have showed no marked deterioration in the device ZT of these elements, as shown in Table 3, below.

**Table 3.**

Type	ZT as made t <sub>anneal</sub> ~ 0 hrs.	ZT after t <sub>anneal</sub> ~ 15 hrs.	ZT after t <sub>anneal</sub> ~ 30 hrs.	ZT after t <sub>anneal</sub> ~ 45 hrs.	ZT after t <sub>anneal</sub> ~ 60 hrs.
P	$1.7 \pm 0.25$	$2.0 \pm 0.25$	$2.25 \pm 0.25$	$2.25 \pm 0.25$	$1.95 \pm 0.25$
N	$0.59 \pm 0.1$	$0.68 \pm 0.1$	$0.84 \pm 0.15$	$0.71 \pm 0.1$	$0.76 \pm 0.15$

Besides superlattices, the device fabrication methodology and the HAF-LIOF aspect of the present invention are applicable to thin substrates from two non-superlattice material systems, GaSb and InAs, corresponding to the bandgaps of the n-SiGe/p-TAGS and n-PbTe/p-TAGS systems. Open-circuit voltage as a function of  $\Delta T$  in a 100 element GaSb and InAs thin-substrate module of the present invention have capable of Voc values of  $\sim 4.5$  Volts to  $\sim 3.5$  Volts and are capable to generate  $\Delta T$  in

excess of 100K, corresponding to active heat fluxes of  $\sim 300 \text{ W/cm}^2$ , needed for achieving high electrical power densities.

### Manufacture of the Thermoelectric Devices and Modules

5        Various methods are available for the manufacturing of the devices and the device components of the present invention. Given below for purposes of illustration are steps and methods involved in fabricating the individual p and n-type thermoelectric pairs of the present invention and are steps and methods for integration of the thermoelectric pairs into modules. The steps and method described below are  
10        illustrative and are not given to imply any limitations on the present invention.

      The thermoelectric materials utilized as the p and n-type thermoelements of the present invention are typically overgrown films on commercial substrates, the overgrown films having a thickness of for example 5 to 20  $\mu\text{m}$ . Substrates for the growth of, for example the thin-film superlattices or other thin film thermoelectric  
15        structures, may have the same conductivity type as the overgrown films or may permit the overgrowth of opposite conductivity type films. The overgrown films can be metallized to provide a low-resistance contact, such as a low-resistance Peltier contact.

      In one fabrication method of the present invention, fabrication of the thermoelectric devices of the present invention is facilitated by inverted-couple  
20        processing. Table 4 shown in Figure 6C illustrates the inverted processing approach of the present invention. In inverted-couple processing, one leg of a p thermoelement and one leg of an n thermoelement are attached a common electrical member adjoining the two elements. Fabricating the individual n-type and p-type thermoelements in each leg  
25        of the thermoelectric power conversion stages can occur in one example of the present invention by forming n-type and p-type films on separate substrates, and then attaching the individual n-type and p-type thermoelements to a common header.

      Alternatively, films of a specific type can be formed on a common substrate and then selectively converting (e.g. by selective ion implantation) different regions of the formed thermoelectric material into n-type and p-type regions. For example, the  
30        thermoelements could be formed intrinsic (or specifically doped) and then type-converted to another (i.e., a p-type to n-type conversion or an n-type to p-type conversion) by for example impurity-diffusion. Type-conversion would then be performed at a convenient stage in the manufacturing process. Regardless of the specific details, a set of p and n-type materials having a pre-arranged pattern are

attached to a common header like SiC, AlN, low-resistivity silicon, and silicon with a thin insulating layer.

In one fabrication method of the present invention, substrates including the individual n-type and p-type thermoelements are separated, for example by scribing or laser dicing, into individual segments. The individual segments are then bonded onto a header such that alternating n-type and p-type conductivity materials exist between each adjacent thermoelement. The surfaces of the header that come in contact with the n- and p-type segments are preferably metallized prior to assembly to provide low-resistance electrical connection between adjacent n- and p-type segments where necessary to electrically interconnect adjacent thermoelements. Likewise, the surfaces of the individual n-type and p-type thermoelements that come in contact with the header are preferably metallized prior to assembly to provide the necessary low-resistance electrical connection to the n-type and p-type thermoelements, else a high electrical contact resistance can limit the efficiency of the thermoelectric stage and the resultant thermoelectric device.

Following bonding of n- and p-type segments, the substrates from each of the p- and n-segments are selectively removed for example by using selective etchants. The thermoelements are then patterned using photolithographic patterning followed for example by etching, or by laser ablation, to produce the desired cross-sectional thermal conduction area for the present invention (i.e., to set the aspect ratio and ultimately determine the packing fraction). Low resistivity contact metallizations are then evaporated on an upper surface of the n- and p-type thermoelements. In this step, either the same metallization can be used for both of the n- and p-type section, or different metallizations can be used (i.e., separate evaporations), depending on the contact resistance requirements. Sheet resistances, or conductances as specified above, associated with the metallizations are designed not to restrict the performance of the thermoelectric devices.

A top, pre-patterned metallization header can, in one embodiment of the present invention, be attached to the metallized sections to function as the aforementioned heat pipe. Alternatively, the header itself prior to metallization can be patterned to provide the aforementioned heat pipe. The formed pair of thermoelements (i.e., the n thermoelement and the p-thermoelement) including the attached header can then be flipped and bonded to a second header. The second header, referred to for the purpose of illustration as a bottom header, thermally connects the n thermoelement to the p-

thermoelement, but contains patterned electrical connections such that electrically the n thermoelement and the p-thermoelement are individually connected, as shown in Figures 1A and 1B. The bottom header thus functions as an electrical member having, as shown in Figures 1A and 1B, a split electrical contact (i.e., an electrical contact only contacting individually the n-type and p-type thermoelements), while as a thermal member the bottom header functions as a continuous thermal contact.

Regardless of the formation approach (i.e. direct deposition or bonding), thick metallizations and patterning can be used, according to one embodiment of the present invention, to form the noted bottom header and to provide the afore-mentioned split electrical contact. Direct attachment by deposition or bonding would permit a large number of patterned thermoelements each possessing the requisite thermal conduction area to be fabricated and electrically connected in series to provide either an output electrical contact for power conversion or for cooling. Subsequent stages of thermoelectric devices could then be added using similar procedures, or by attaching subsequent pre-fabricated stages, or by attaching selective members of subsequent stages.

One illustrative example of inverted couple processing is given below:

P-type and n-type superlattice thermoelectric films are deposited on GaAs substrates. The deposited superlattice films are patterned with Cr/Au/Ni/Au metallizations. The deposited superlattice films and/or the GaAs substrates are etched in preparation for dicing. Diced strips of the p-type and n-type superlattice films attached to the GaAs substrates are then bonded in an alternating conductivity type pattern to a header. The header includes an AlN substrate having Ti/Au metallization (annealed) and having a subsequent Cu/No/Au topmost metallization. A Sn preform bonds the diced strips to the AlN substrate (functioning as a first header). The GaAs substrate is then etch removed, and Cr/Au/Ni/Au contacts are evaporated through shadow masks or evaporated and patterned to form electrical contacts to the superlattice thin films. Thick metal pads are then formed on the evaporated contacts to define for example a heat pipe structure. Dies containing the superlattice thin films and the attached AlN header are placed and bonded to a separate split metallized header (functioning as a second header) allowing for individual electrical connection to each of the n- and p-type thin film thermoelements.

By way of example, Table 5 depicts various bonding steps used to fabricate the three stage device shown in Figure 2.



- As depicted in Table 5, in stage 3 of the thermoelectric device (i.e. the uppermost header), a preferred heat spreader is AlN or Si. In this stage, a AgCu eutectic is used as a solder material for bonding the heat spreader to the metallization layers on the afore-mentioned N-SiGe/P-TAGS thermoelements. Metallization layers on the N-SiGe/P-TAGS thermoelement pair include silver having a typical diffusion barrier layer of W or Mo or Ni or similar refractory metal to prevent diffusion of Ag into the N-SiGe and P-TAGS materials.

Table 5

STEP	BONDING PROCESS	Heat Spreader	Solder Material	Interconnect Metallization and Resistivity at Mean Operating Temperature	Solder Diffusion Barriers
1	In Stage 3 of the Cascade: 1050K	AlN or Si	AgCu (72/28) Eutectic	Silver ( $\rho \sim 4.5 \mu \text{ Ohm-cm}$ )	W (sputtered)
2	In Stage 2 of the Cascade: 800K	AlN	AgAuGe (45/38/17) Eutectic	Silver ( $\rho \sim 3.3 \mu \text{ Ohm-cm}$ )	Mo (E-beam)
3	In Stage 1 of the Cascade: 505K*	SiC	Sn	Copper ( $\rho \sim 2.3 \mu \text{ Ohm-cm}$ )	Ni (E-beam or plated)
4	Of heat Source to Stage 3 at 975K	N/A	AgCuP (15/80/5)	N/A	N/A
5	Of Stage 2 to Stage 3 (with Heat Source) at 738K	N/A	AuIn (75/25)	N/A	N/A
6	Of Stage 1 to Stage 2 (with Stage 3 and Heat source) at 490K	N/A	SnAu (90/10)	N/A	N/A
7	Of Heat sink to bottom of Stage 1 at 395K	N/A	InSn (52/48)	N/A	N/A

As depicted in Table 5, in stage 2 of the thermoelectric device, a preferred heat spreader is AlN. In this stage, a AgAuGe eutectic is used as a solder material for bonding the heat spreader to the metallization layers on the afore-mentioned N-PbTe/P-TAGS thermoelement pair. Metallization layers on the N-PbTe/P-TAGS

- 5 thermoelement pair include silver having a typical diffusion barrier layer of Ni or W or Mo to prevent diffusion of Ag into the N-PbTe and P-TAGS materials.

- As depicted in Table 5, in stage 3 of the thermoelectric device, a preferred heat spreader is SiC. In this stage, a Sn eutectic is used as a solder material for bonding the heat spreader to the metallization layers on the afore-mentioned n- and p-type Bi<sub>2</sub>Te<sub>3</sub>-superlattice-thin-film pair. Metallization layers on the n- and p-type Bi<sub>2</sub>Te<sub>3</sub>-superlattice-thin-film pair include Cu having a diffusion barrier layer of Ni or a similar metal to prevent diffusion of Cu into the N-Bi<sub>2</sub>Te<sub>3</sub> SL and/or P-type Bi<sub>2</sub>Te<sub>3</sub> SL materials.
- 10

- As depicted in Table 5, the uppermost stage (i.e. stage 3) can be bonded to the heat-source header (e.g., a Cu plate) using a AgCuP eutectic bond. Stages 2 and 3 can be eutectic bonded together using a AuIn eutectic. Stages 1 and 2 can be eutectic bonded together using a SnAu eutectic. Stage 1 can be bonded to the heat-sink header (e.g., an Al plate) using an InSn eutectic bond. Hence, in the present invention, successively-lower-melting-point eutectics bond the successive stages so that the previously-bonded stages are in tact. Such measures serve to match or reduce the mismatch in the coefficients of thermal expansion between the various stages as successive bonding can cause thermal stress.
- 15
- 20

- An example of stacking of the various stages to obtain efficient thermal interfaces between each of the adjacent stacks by using eutectic metal bonding is described by R. Venkatasubramanian *et al* in Appl. Phys. Lett., Vol. 60, 886 (1992), the entire contents of which are incorporated by reference.
- 25

### **Integration of Thermoelectric Devices and Modules to Semiconductor Chip Packages**

- A thermoelectric device of the present invention can be attached to an integrated circuit die or wafer element (preferably to the backside) with or without an intervening layer of thermal grease or plastic adhesive. For direct attachment without intervening layers of thermal grease or plastic adhesive, a thin electrically insulating layer or a series of back-side p-n isolation junctions can be utilized to permit electrical isolation of the
- 30

integrated circuit on the die from the currents flowing in the thermoelectric devices. In this approach, the "top" header joining the thermoelectric device of the present invention to the integrated circuit die is made of thick metallizations which form the electrical contact and the heat pipe to the p-n thermoelements. Suitable thermoelectric materials deposition/attachment/formation, type conversion, and patterning form the p-n thermoelements and the heat pipe structures. Subsequent metallizations complete a "bottom" header and provide in one embodiment of the present invention a place for attachment to a heat sink device (e.g., an air-cooled plate or a heat-pipe)

Figure 7A is a schematic depicting the bonding of a pre-fabricated thermoelectric device 72 to a semiconductor device chip 74. In this approach, bonding is used to bond the pre-fabricated thermoelectric devices to an integrated circuit die. As such, this approach separates the thermoelectric device fabrication steps from the semiconductor device chip. In this approach, a number of bonding techniques (to be discussed below) can be used to join an upper header 75 of the pre-fabricated thermoelectric device 72 to the semiconductor device chip 74. Accordingly, in the attached structure, heat from power dissipating devices 76 in the semiconductor device chip 74 will be pumped through the thermoelements 73 and dissipated at a heat sink (not shown) attached to the lower header 77.

Figure 7B is a schematic depicting the attachment of the present invention of a thermoelectric device without a top header onto a semiconductor device chip. Specifically, Figure 7B depicts the bonding of pair of thermoelements 73 to the semiconductor device chip 74. As shown in Figure 7B, the bonding to the semiconductor device chip 74 is facilitated by the pre-deposition or growth of an electrically insulating layer 82 on the semiconductor device chip 74 (e.g. silicon dioxide formation on a Si device wafer). As shown in Figure 7B, the semiconductor device chip 74 itself serves as a header spreading heat from power dissipating devices 76. Thus, in this embodiment of the present invention, the thermoelements are attached directly to the semiconductor device chip 74 without the utilization of a top header.

Figure 7C is a schematic depicting the sequential formation of a thermoelectric device 72 on the present invention onto a semiconductor device chip 74. In this approach, the fabrication process of the present invention may utilize bonding at separate steps in the process to bond thermoelectric materials and/or superlattice layers to other layers of the thermoelectric device, and to provide a mechanism for direct

attachment of the thermoelectric devices of the present invention to the semiconductor device chip 74.

In the simplified process depicted in Figure 7C, at step (a), an electrically insulating layer 82 is formed on the semiconductor device chip 74. The layer 82 can be a thermal oxide grown on a Si device chip; the layer 82 can be a deposited oxide such as  $\text{SiO}_2$  or  $\text{Si}_3\text{N}_4$  deposited for example by sputtering or vapor deposition. At step (b), metallizations 83 (including interconnections between the thermoelements not shown for the sake of simplicity) are deposited and patterned in accordance with the layout of the thermoelectric devices 72 on the semiconductor device chip 74. The metallizations 83 can include for example structures to form the heat pipe 5, described in Figure 1. At step (c), pair of thermoelements 73 are attached (deposited or bonded) to the metallizations 83. The pair of thermoelements 73 can include for example the features of thermoelectric device 1 shown in Figure 1. At step (d), a set of metallizations 85 are formed on thermoelements 73. At step (e), contact and annealing using the procedures detailed below complete the fabrication by joining a header 84 to the metallizations 85.

Accordingly, various approaches of the present invention include:

- (1) attaching a pre-fabricated thermoelectric module to a device wafer,
  - (2) building a thermoelectric device from the backside of a device wafer, or
  - (3) building a part of a thermoelectric device onto the backside of a device wafer
- (e.g. building heat pipes onto the backside of a device wafer), and completing fabrication by attachment of remaining pre-fabricated components.

For attachment, several attachment methods can be used including: (1) soldering, (2) brazing, (3) friction bonding, and (4) insulator-insulator bonding similar to wafer bonding. Furthermore, in a preferred embodiment, a hybrid "reactive" bonding process is utilized in which insulator surfaces, having a thin reactive metal layer, are placed opposed to one another and then contacted and heated to react the metal layer with the insulator surfaces and thereby bond the opposed components together. Such a metal include for example Ti, W, Cr, Mo, etc., or alloys thereof. These metals readily oxidize and form in a preferred embodiment silicides which melt at temperatures of  $300^\circ\text{C}$  or less. The hybrid reactive bonding process of the present invention relies on the reactivity of the thin metal layer with the respective insulators to achieve a bond. In one embodiment of the present invention, the metal layer is preferably thin (e.g., less than  $500\text{\AA}$ ) such that all of the reactive layer is consumed, or reacts with, the insulating layers. In hybrid reactive bonding, bonding is achieved when the surfaces are brought

into contact and then heated such that the metal reacts with one or both insulating surfaces.

Furthermore, friction bonding according to the present invention can be used to bond thermoelectric materials and/or superlattice layers to other layers on the thermoelectric device and provide a mechanism for direct attachment of the thermoelectric devices of the present invention to an integrated circuit die or wafer element. Friction bonding can, in one embodiment of the present invention, be implemented with intervening reactive layers. In friction bonding, linear motion over a short distance using an ultrasonic transducer provides the friction necessary to produce heating at the surface that will produce the bond. Heating to a high fraction of the melting temperature and then using a friction bonding technique to produce local heating and thereby for instance melting or plastic deformation at the contact surfaces can produce a suitable bond. Heating from one direction and cooling from another side can be used to locally heat to a small area near the contact surfaces. Small amounts of material or thin sheets of material in a perform cut to die or strip size to match the thermoelectric component parts.

Materials in thin sheets or thin film form are used, according to the present invention, to provide for a buffer that protects the thermoelectric superlattice materials during the friction bonding. Materials in thin sheets avoid mechanical damage to the top layers of the thermoelectric materials. The thin layer is selected to form a eutectic that allows friction bonding. In friction bonding, the surfaces of the materials to be bonded can be roughened if necessary to improve the friction and thus the efficacy of forming a friction bond.

Further, diffusion bonding or thermal annealing can be used to bond the thermoelectric devices to a semiconductor device chip.

Bonding can occur between a top header of a thermoelectric devices and a semiconductor device chip by any number of the processes described herein, and can utilize a bonding material to facilitate coupling of the semiconductor device chip to the semiconductor device chip. Regardless of approach, a thermally conductive and mechanically stable connection or bond is preferred between the top header and the semiconductor device chip. Bonding to the semiconductor device chip to the thermoelectric devices of the present invention can be accomplished in the following non-limiting examples by:

1. utilization of thermal adhesives or thermally conductive epoxy,

2. soldering,
3. diffusion bonding using electroplated or evaporated metal contacts,
4. utilization of anisotropic thermal adhesives,
5. utilization of thermoplastic conductive polymers, and
- 5 6. utilization of silicon to silicon molecular bonding (in the case where the cooling header of the thermoelectric device is made from silicon).

Heat flux from the semiconductor device chip can be dissipated from the thermoelectric devices of the present invention by a heat sink operating at a temperature above that of the semiconductor device chip. Moreover, once bonded, the attached  
10 thermoelectric devices of the present invention, when not cooling, can sense a heat flux from the chip and thus can provide active sensing of the device chip performance. A template of such thermoelectric devices can therefore, in one embodiment of the present invention, provide a mapping of device component utilization (i.e. those device components having higher utilizations will produce higher amounts of heat flux into the  
15 proximate thermoelectric devices).

Thus, as illustrated above, the present invention can utilize a number of approaches using bonding to facilitate thermal transfer by thermal conduction from one thermoelectric power conversion stage to another. Such techniques and other techniques known in the art can be used to appropriately bond the various stages  
20 together. These approaches, according to the present invention, realize high-quality thermal interfacing.

Another alternative approach of the present invention for integrating the various thermoelectric conversion stages utilizes radiant thermal energy transfer using Purcell-enhancement cavity transmitter/receiver structures such as those described in the afore-  
25 mentioned U.S. Provisional Application No. 60/253,743, the entire contents of which are incorporated herein by reference, entitled "Spontaneous emission enhanced heat transport method and structures for cooling, sensing, and power generation" for heat transfer from one thermoelectric power conversion stage to another. In this approach, the radiant portion, if not the dominant process, plays a substantial role in managing  
30 thermal stress by providing less-rigidly-bonded interfaces. Figure 9 is a schematic illustration in which radiant coupling is used between adjacent thermoelectric conversion stages.

As shown in Figure 8 a heat source 14 is coupled via radiant coupling mechanism 216 to a thermoelectric stage 16. Stage 16 is in turn coupled via radiant

coupling mechanism 217 to the thermoelectric stage 17. Stage 17 is in turn coupled via radiant coupling mechanism 218 to the thermoelectric stage 18. Electrical connections 220 provide connections to the thermoelements on each stage.

Further, the present invention can utilize Purcell enhancement from an enhanced density of radiative modes in small-scale structures (similar to enhanced electronic density of states in quantum-confined systems) for enhanced spontaneous emission using patterned /  $\mu\text{m}$ -size-range, appropriately-spaced, structures for specific temperatures, on the heat spreader. Thus, engineered micro-fins can also potentially enhance spontaneous radiative heat transport. These  $\mu\text{m}$ -size geometries are achievable with photolithography a large-area wafers for a cost-effective implementation.

Spontaneous emission enhanced heat transport (SEEHT) may additionally enhance emission at infra-red wavelengths near 300K. The incorporation of micron or sub-micron size Purcell cavities, will provide for the theoretical maximum radiative emission at peak wavelengths of 10  $\mu\text{m}$  which will enhance heat transport by as much as a factor of 1000 at 300K, leading to a radiative dissipative flux of  $\Phi_{\text{SEEHT}}$  of  $44\text{W}/\text{cm}^2$ . Such micron size particles incorporated by impregnation or self-assembly, followed by overgrowth, permit the scope for radiative heat transfer mechanisms to be considerably enhanced. Such particles can further be incorporated in high-thermal conductivity heat spreader such as SiC, AlN, Si, diamond, etc. Enhancement of such intensities, even compared to highly-emissive (Ti) surfaces, showing both structure dependence and wavelength dependence, is shown in Figure 9. Indeed, Figure 9 is a plot of apparent emission intensity as a function of the surface temperature of different engineered structures according to the present invention. As such, in one embodiment of the present invention, a radiative coupling mechanism includes a thermally conductive layer having dispersed therein particles including one of metal, semimetal, and semiconductor particles to thereby enhance black body radiation from the thermally conductive layer and support radiative heat transfer across the interfaces of the thermoelectric device components without the necessity of physical bonding.

While not limited to the following theory, the present invention recognizes that of enhanced emission with these Purcell cavity structures can be further enhanced/realized if there is matching of "increased density of states" in emitters with "increased density of states" with receivers/absorbers, i.e., resonant thermal energy transfer. In addition to "resonant thermal energy transfer" by Purcell-cavity effects,

other "proximity coupling of radiative infrared modes" can be exploited as well, in the present invention. Utilization of radiation coupling will, according to the present invention, reduce thermal stress, by removing (strong) physical interfacial contacts between various stages. Further, the mechanical alignment of the resonant structures will not be a significant issue, given that the typical size of the inverted couple headers are  $\sim 300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$ .

### Thermoelectric Modules

For automatic assembly of the modules described above a dicer and pick-and-place tools (standard to the IC industry) can be used. A wafer dicer and robotic pick-and-place tool, provide not only cost-effective but also reliable fabrication of both mini-modules and large-scale modules. The tool is used to dice p-n couple dies from a processed wafer and to assemble these inverted couple dies into a range of devices, from mini-modules to large-array of mini-modules. The dicer and pick-and-place tools, described above can also be used according to the present invention to assemble thin-substrate (i.e.  $100\text{ }\mu\text{m}$  to  $250\text{ }\mu\text{m}$  thick) bulk modules as well as substrate die containing the afore-mentioned superlattice thin-film structures.

In one aspect of the present invention, large-scale headers are used, on which a large array of mini-modules are assembled to produce large-scale modules and proportionally larger powers.

Figure 10 is a schematic arrangement of a three stage or unit thermoelectric device of the present invention having a split-header on a lower stage **18** to provide thermal expansion relief. In another aspect of the present invention, the lower-stage **18** of the multi-stage thermoelectric device can be nearly instantly converted to a heat pump for short periods of time, thus avoiding catastrophic device damage due to for example an interruption in coolant flow, and further enhancing reliability. As such, Figure 10 represents a multi-stage thermoelectric device of the present invention in which electrical reconfiguration avoids catastrophic failures during coolant flow loss to the lower stage **18** and thus the risk of deterioration of the thermoelectric properties of the thermoelements at this stage (i.e., due to deterioration of the thermoelectric materials and/or contacts) is minimized.

An electrical configuration for permitting avoidance of a catastrophic failure is depicted in Figure 11. Figure 11 is an electrical diagram showing an exemplary



configuration for operating a thermoelectric device of the present invention in either a heat pump mode or a power conversion mode. As shown in Figure 11, each stage of a thermoelectric device 102 is temperature monitored by temperature monitor block 104. Each stage is electrically controlled/sensed by a switch block 106 and a controller 108.

- 5 In a power conversion mode, the controller 108 supplies power out from the thermoelectric device 102. The controller can include filters and dc-ac converters to output ac power or can include dc-dc power converters to output higher voltage dc power than directly available from the thermoelectric device 102. Figure 12 depicts a cooling system 110 which for illustrative purposes depicts a heat exchanger 112 utilized to pump with pump 114 a fluid to a heat sink plate 116. A flow sensor 118 monitors the flow of coolant to the heat sink plate 116. A temperature of the lower stage and the output power from the lower stage is monitored by a power unit 120. In the event of coolant failure, the controller 108 can electrically reconfigure the thermoelectric device from a power conversion mode to a heat pump mode. As a result, heat will be pumped to the heat source upon this electrical reconfiguration permitting the temperature of the lower stage devices to at least momentarily avoid overheating and catastrophic destruction. Once the coolant failure is restored, or in the event of permanent failure of the cooling system 110, the thermoelectric device can continue in the "cooling" mode until the heat source is turned off, removed, or otherwise decoupled from the thermoelectric device 102. As such, catastrophic failures can be avoided.

- Further, the controller 108 being connected to the separate stages can switch the stages from the above-noted power conversion mode and heat pump (i.e. a cooling mode) to a heat flux sensing mode. In a heat sensing mode, the current through the thermoelements are measured as an indicator of the heat flux through the thermoelements coming from a heat source. Such information can be used as a measure of the heat being dissipated from the heat source. The controller can thus process a signal indicative of heat flux from the thermoelectric pair of n-type and p-type thermoelements.

- Thus, the controller of the present invention connected electrically to the thermoelectric devices of the present invention can be configured to switch the thermoelectric devices between at least one of a cooling mode, a heat pump mode, a power conversion mode, and a heat flux sensing mode.

### Electronics Application

Accordingly, integration of the thermoelectric devices and thermoelectric device modules of the present invention to electronic devices such as semiconductor chip packages can be accomplished through a number of mechanisms. Thermoelectric devices can be coupled to such devices for the purposes of "hot spot" cooling those parts of the device most susceptible to exceeding operational temperature limits.

Integrated semiconductor devices requiring hot spot cooling include for example microprocessors, graphic processors and other power dissipating devices fabricated in silicon, germanium, silicon-germanium, gallium arsenide, or any such semiconductor material. The integration can occur for example via recesses in the semiconductor chip and/or in the headers. In this approach, vertical and lateral vias or recesses are fabricated in the semiconductor chip and/or the heat spreader. The above-noted bonding techniques join the semiconductor chip to the heat spreader.

Figure 12A is a schematic depicting a coupling structure for coupling a thermoelectric device of the present invention to a semiconductor device chip. Specifically, Figure 12A depicts a thermoelectric device attached to a semiconductor device chip 74. The semiconductor device chip 74 includes the aforementioned power dissipating devices 76 in a region proximate to the recesses 78. Selective cooling occurs via the cooling of recesses 78 in the semiconductor device chip 74. The recesses 78 permit alignment of the thermoelectric devices 72 to the power dissipating devices 76.

Further, an electrically insulating interlayer 82 can be preferably interposed between the thermoelectric devices and the semiconductor material of the chip. As noted previously, the properties of the electrically insulating interlayer 82 are such to permit electrical isolation without impeding heat flux between the semiconductor device chip 74 and the thermoelectric devices. An electrically insulating material such as  $\text{SiO}_2$  can be suitable for the electrically insulating interlayer 82, although other insulating materials known in the art are likewise applicable. The electrically insulating interlayer 82 is at least applied to the semiconductor chip in regions where the thermoelectric devices are to be attached. Following application, metallized contacts 83 can be made on the electrically insulating interlayer 82 to provide electrical connections to the thermoelectric devices. Metallized contacts can be made using one or more of known metallization techniques such as for example but not limited to evaporation, electroplating, or soldering. Following metallization, diffusion bonding, or thermal annealing can be used to bond the thermoelectric devices to the chip.

Bonding occurs between a top header 79 of the thermoelectric devices and the semiconductor device chip 74 by any number of the processes described above, and can utilize a bonding material 80 to facilitate coupling of the semiconductor device chip 74 to the semiconductor device chip 74. Regardless of approach, a thermally conductive and mechanically stable connection or bond is preferred between the top header 79 and the semiconductor device chip 74.

Heat flux from the semiconductor device chip 74 is dissipated from the thermoelectric devices 72 by a heat sink operating at a temperature above that of the semiconductor device chip 74. As such, heat flux from the power dissipating devices 76 is more efficiently dissipated to the outside environment due to the higher temperature differential existing between the temperature of the heat sink and the ambient than the temperature of the semiconductor device chip 74 and the ambient.

Figure 12B is a schematic depicting another coupling structure for coupling a thermoelectric device to a semiconductor device chip. As shown in Figure 8B, the thermoelectric devices 72 can be directly attached to the semiconductor device chip 74 without utilization of recesses 78. In this coupling structure, placement of the thermoelectric devices 72 on the semiconductor device chip 74 aligns the thermoelectric devices 72 opposite the power dissipating devices 76.

Thus, coupling of thermoelectric devices 72 to the semiconductor device chip 74 occurs with or without the utilization of recesses. Figure 13 is a schematic depicting another coupling structure for coupling a thermoelectric device to a semiconductor device chip. As shown in Figure 13, thermoelectric devices 72 are attached in recesses 78 existing in both the semiconductor device chip 74 and a heat spreader plate 90. The heat spreader plate 90 can utilize a bonding material 80 to couple the heat spreaders 84 to the heat spreader plate 90.

Figure 14 is a schematic depicting another coupling structure for coupling thermoelectric devices to a semiconductor device chip. The coupling structure includes vias for electrical connections to the thermoelectric devices. Power requirements for the thermoelectric devices require that electrical leads to the thermoelectric devices be electrically insulated. As shown in Figure 14, the electrical leads 92 can be integrated directly in a header (e.g. header plate 90) by vias 94, which either vertically or laterally provide electrically conductive channels. The vias 94 can be either etched or pre-fabricated such that the vias 94 run through the header plate 90. Insulating material 96 for the vias 94 can be any high temperature plastic or ceramic of sufficient dielectric

quality which encapsulates metal (e.g., copper, gold or, any high electrically conductive metal). Vias in the header plate **90** can be created by laser ablation and can have electroplated metal deposited therein. This structure shown in Figure 14 having insulated electrical leads facilitates independently power or sensing of individual ones of the thermoelectric devices. The header plate **90** would be made of materials that match the coefficient of thermal expansion of silicon (e.g. within a 5% match in terms of linear expansion coefficient).

Figure 15 is a schematic depicting another coupling structure for coupling thermoelectric devices to a semiconductor device chip. The coupling structure includes vias for electrical connections to the thermoelectric devices and includes high thermal conductivity materials in the header plate **90**. A combination of high thermal conductive materials **98** like highly oriented pyrolytic graphite, carbon foams, graphite foams can be used to enhance the rejection of heat from the hot side of the thermoelectric device. These materials can be used as a part or for the entirety of the heat spreader plate **90**. Thermal conductivity of these materials can be five times that of the thermal conductivity of copper. These materials would be extremely efficient in dissipating heat from the heat sink **84** of the thermoelectric devices **72**. As illustrated in Figure 15, lateral electrical connections **100** connect to the thermoelectric devices **72**. The lateral electrical connections **100** like the electrical leads **92** are formed with electrically conductive materials and insulated from the heat sink plate **90**.

Numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

**CLAIMS:**

1. A thermoelectric device comprising:  
at least one thermoelectric unit comprising,  
5 at least one thermoelectric pair of n-type and p-type thermoelements,  
a first header coupled to one side of the thermoelectric pair,  
a second header coupled to a second side of the thermoelectric pair, and  
said thermoelectric pair having a thermal conduction channel area smaller than  
an area of at least one of the first header and the second header such that the thermal  
10 conduction area is a fraction of the area of said at least one of the first header and the  
second header, and said fraction is less than 50%.
  2. The device of Claim 1, wherein said fraction is less than 20%
  3. The device of Claim 1, wherein said fraction is less than 10%.
  4. The device of Claim 1, wherein said fraction is less than 1%.
  - 15 5. The device of Claim 1, wherein said fraction is less than 0.5%.
  6. The device of Claim 1, further comprising:  
a thermal impedance increasing device disposed between the thermoelectric pair  
and one of said first and second headers and configured to set a thermal impedance  
across a gap between the first and second headers to be at least comparable to a thermal  
20 impedance across said thermoelectric pair.
    7. The device of Claim 6, wherein the thermal impedance increasing device  
comprises:  
a heat pipe disposed between one of said first and second headers, coupled to  
said thermoelectric pair, and elongated in a transverse direction to space apart the first  
25 header from the second header.
    8. The device of Claim 7, wherein the heat pipe comprises:  
a metal member disposed between said thermoelectric pair and one of said first  
and second headers, extending in said transverse direction, and having a width  
comparable to a width of the thermoelectric pair.
    - 30 9. The device of Claim 7, wherein said heat pipe is configured to separate said  
first header from said second header by a distance such that a thermal impedance across  
a gap between the first and second headers is at least comparable to a thermal  
impedance across the thermoelectric pair.
    10. The device of Claim 9, wherein said distance is at least 100 to 500  $\mu\text{m}$ .

11. The device of Claim 9, wherein said distance is at least 10  $\mu\text{m}$ .

12. The device of Claim 6, wherein the thermal impedance increasing device comprises:

5 an evacuated housing enclosing the thermoelectric pair and said one of the first and second headers.

13. The device of Claim 12, wherein said housing comprises a vacuum level of no greater than 1 Torr.

14. The device of Claim 6, wherein the thermal impedance increasing device comprises:

10 a housing enclosing the thermoelectric pair and said one of the first and second headers, said housing filled with a low thermal conductivity medium to reduce a thermal impedance across a gap between the first and second headers to be at least comparable to a thermal impedance across the thermoelectric pair.

15 15. The device of Claim 14, wherein said low thermal conductivity medium comprises Ar gas.

16. The device of Claim 1, wherein said thermoelectric pair, upon conduction of said heat through the thermoelements, produces an electrical potential.

17. The device of Claim 1, wherein said thermoelectric pair, upon a current flow through the thermoelements, cools said first header.

20 18. The device of Claim 1, further comprising:

electrical connections to said thermoelectric pair, having a resistance less than  $1/10^{\text{th}}$  of an Ohmic resistance of the thermoelectric pair.

19. The device of Claim 18, wherein said electrical connections comprise metal connections.

25 20. The device of Claim 19, wherein said metal connections comprise Cr/Au/Ni/Au contacts to said thermoelectric pair.

21. The device of Claim 1, wherein said thermoelectric pair comprises: a thermoelectric material having a figure of merit of at least 1.

30 22. The device of Claim 1, wherein said thermoelectric pair comprises: a thermoelectric material having a figure of merit of at least 2.

23. The device of Claim 1, wherein said thermoelectric pair comprises: at least one of a superlattice and a quantum dot superlattice.

24. The device of Claim 23, wherein said superlattice comprises:

at least one of a  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  superlattice, a  $\text{SiGe}$  superlattice, and a  $\text{PbTe/PbSe}$  superlattice.

25. The device of Claim 1, wherein at least one of said first header and second header comprises:

5 a thermally conducting member.

26. The device of Claim 25, wherein the thermally conducting member comprises:

an electrically conducting member and an electrical insulation member formed on the electrically conducting member; and

10 a patterned conductor formed on the electrical insulation member and connecting to said thermoelectric pair.

27. The device of Claim 26, wherein said electrically conducting member comprises at least one of Al, Cu, doped Si, and doped SiC.

28. The device of Claim 26, further comprising:  
15 plural thermoelectric pairs connected in series by said patterned conductor.

29. The device of Claim 25, wherein the thermally conducting member comprises:

an electrically insulating plate; and

20 a patterned conductor provided on the electrically insulating plate and connecting to said thermoelectric pair.

30. The device of Claim 29, wherein said electrically insulating plate comprises at least one of AlN, SiC, Si, and diamond.

31. The device of Claim 29, further comprising:  
plural thermoelectric pairs connected in series by the patterned conductor.

25 32. The device of Claim 3, wherein the heat pipe has a thermal conduction channel area that is smaller than an area of said one of the first header and the second header.

33. The device of Claim 3, wherein the heat pipe comprises a heat pipe having a temperature drop of less than 5K for heat fluxes in a range about  $25 \text{ W/cm}^2$ .

30 34. The device of Claim 3, wherein the heat pipe comprises a heat pipe coupled to said thermoelectric pair and said one of the first and second headers by a metal bond.

35. The device of Claim 34, wherein the metal bond comprises at least one of a solder-bump-bond, a friction bond, and a reactive-metal bond.

36. The device of Claim 3, wherein the heat pipe comprises a radiative coupling mechanism coupling heat from the heat pipe to at least one of said first header, said thermoelectric pair, and said second header.

37. The device of Claim 36, wherein the radiative coupling mechanism  
5 comprises a Purcell-enhancement cavity transmitter/receiver structure.

38. The device of Claim 37, wherein the Purcell-enhancement cavity transmitter/receiver structure comprises:

a thermally conductive layer including dispersed therein one of metal, semimetal, and semiconductor particles.

39. The device of Claim 37, wherein the Purcell-enhancement cavity  
10 transmitter/receiver structure comprises:

at least one of  $\mu\text{m}$ -size and sub-micron-size radiation fins configured to enhance spontaneous radiative heat transport.

40. The device of Claim 1, further comprising:

a controller configured to control a current through said thermoelectric pair such  
15 that said thermoelectric device operates in at least one of a cooling mode, a heat pump mode, a power conversion mode, and a heat flux sensing mode.

41. The device of Claim 40, wherein said controller is configured in said heat flux sensing mode to measure said current through said thermoelectric pair.

42. The device of Claim 1, wherein said second header comprises:  
20 a body having slits formed partially through the body.

43. The device of Claim 1, wherein said second header comprises a material having a thermal conductivity higher than Cu.

44. The device of Claim 1, wherein said first header comprises:

an integrated circuit element; and

a heat spreader disposed between said integrated circuit element and said thermoelectric pair.

45. The device of Claim 1, wherein said at least one thermoelectric unit is configured to have a specific power greater than 1 W/gm.

46. The device of Claim 1, wherein said at least one thermoelectric unit is configured to have a specific power in a range of 0.0001 W/gm to 0.01 W/gm.

47. The device of Claim 46, wherein the first header is coupled to a heat source in a range of 30-40°C.



48. The device of Claim 1, wherein said at least one thermoelectric unit is configured to produce a power density greater than  $0.5 \text{ W/cm}^2$ .

49. The device of Claim 1, wherein said at least one thermoelectric unit is configured to produce a power density in a range from  $0.0005 - 0.5 \text{ W/cm}^2$ .

5 50. A thermoelectric device comprising:  
plural cascaded thermoelectric units, each unit including,  
at least one thermoelectric pair of n-type and p-type thermoelements,  
a first header coupled to one side of the thermoelectric pair,  
a second header coupled to a second side of the thermoelectric pair,  
10 said at least one thermoelectric pair having a thermal conduction channel area smaller than an area of at least one of the first header and the second header and the thermal conduction area is a fraction of the area of said at least one of the first header and the second header, and  
said fraction is less than 50%.

15 51. The device of Claim 50, wherein one of said plural cascaded thermoelectric units comprises:

at least one upper thermoelectric unit coupled to a heat source;  
at least one lower thermoelectric unit coupled to the at least one upper thermoelectric unit; and  
20 a heat sink thermally coupled to the at least one lower thermoelectric unit and configured to dissipate heat from the at least one lower thermoelectric unit.

52. The device of Claim 51, wherein said fraction in said at least one upper thermoelectric unit is in a range from 80% to 10%.

25 53. The device of Claim 51, wherein said fraction in said at least one lower thermoelectric unit is in a range from 20% to 0.5%.

54. The device of Claim 51, wherein said fraction in said at least one lower thermoelectric unit is less than 0.5%.

30 55. The device of Claim 51, wherein said thermoelectric pair in at least one of the at least one upper thermoelectric unit and the at least one lower thermoelectric unit comprises:

at least one of  $\text{Bi}_2\text{Te}_3$ ,  $\text{Sb}_2\text{Te}_3$ ,  $\text{SiGe}$ ,  $(\text{AgSbTe}_2)_{1-x}(\text{GeTe})_x$ ,  $\text{PbTe}$ ,  $\text{PbSe}$ ,  $\text{ZnSb}$ , and skutterudites.

56. The device of Claim 55, wherein the  $(\text{AgSbTe}_2)_{1-x}(\text{GeTe})_x$  comprises a GeTe mole fraction of  $\sim 0.80$  to  $0.85$ .

57. The device of Claim 51, wherein the at least one upper thermoelectric unit is configured to operate at temperatures from 670K to 870K.

58. The device of Claim 51, wherein the at least one lower thermoelectric unit is configured to operate at temperatures from 470K to 670K. [

5 59. The device of Claim 51, wherein the at least one lower thermoelectric unit is configured to operate at temperatures from 300K to 470K.

60. The device of Claim 51, wherein said plural cascaded thermoelectric units are configured to have a specific power greater than 1 W/gm.

61. The device of Claim 51, wherein said plural cascaded thermoelectric units  
10 are configured to have a specific power in a range of 0.0001 W/gm to 0.01 W/gm.

62. The device of Claim 61, wherein the first header is coupled to said heat source in a range of 30-40°C.

63. The device of Claim 51, wherein said plural cascaded thermoelectric units are configured to produce a power density greater than 0.5 W/cm<sup>2</sup>.

64. The device of Claim 51, wherein said plural cascaded thermoelectric units  
15 are configured to produce a power density in a range of 0.0005 W/cm<sup>2</sup> to 0.5 W/cm<sup>2</sup>.

65. A thermoelectric device comprising:

at least one thermoelectric pair of n-type and p-type thermoelements having a  
doping concentration in respective of said n-type and p-type thermoelements ranging  
20 from  $1 \times 10^{19}$  to  $6 \times 10^{19}$ /cm<sup>3</sup>;

a first header coupled to one side of the thermoelectric pair; and

a second header coupled to a second side of the thermoelectric pair..

66. The device of Claim 65, wherein at least one said n-type and p-type thermoelements have a ZT of greater than 1.

67. The device of Claim 66, wherein at least one said n-type and p-type thermoelements comprise a superlattice structure.

68. A system for thermoelectric power conversion, comprising:

a thermoelectric pair of n-type and p-type thermoelements;

a first header coupled to one side of the thermoelectric pair;

30 a second header coupled to a second side of the thermoelectric pair;

said thermoelectric pair having a thermal conduction channel area smaller than an area of at least one of the first header and the second header such that the thermal conduction area is a fraction of the area of said at least one of the first header and the second header, said fraction being less than 50%; and

a heat sink coupled to the second header and configured to dissipate heat at a rate which maintains a temperature of the second header below a temperature of the first header.

69. The system of Claim 68, wherein said fraction is less than 20%

5 70. The system of Claim 68, wherein said fraction is less than 10%.

71. The system of Claim 68, wherein said fraction is less than 1%.

72. The system of Claim 68, wherein said fraction is less than 0.5%

73. The system of Claim 68, further comprising:

a coupling member coupling the first header to a heat source.

10 74. The system of Claim 73, wherein said coupling member comprises at least one of a steam pipe, a combustion exhaust pipe, and a thermally conducting member having a thermal conductance of at least  $Al$  and extending from said first header to said heat source.

75. The system of Claim 68, further comprising:

15 a thermal impedance increasing device disposed between the thermoelectric pair and one of said first and second headers

76. The system of Claim 68, further comprising:

plural cascaded thermoelectric units, each comprising said first header, said thermoelectric pair, and said second header.

20 77. The system of Claim 76, wherein one of said plural cascaded thermoelectric units comprises:

at least one upper thermoelectric unit coupled to a heat source;

at least one lower thermoelectric unit coupled to the at least one upper thermoelectric unit; and

25 a heat sink thermally coupled to the at least one lower thermoelectric unit and configured to dissipate heat from the at least one lower thermoelectric unit.

78. The system of Claim 77, wherein said thermoelectric pair in at least one of the at least one upper thermoelectric unit and the at least one lower thermoelectric unit comprises:

30 at least one of  $Bi_2Te_3$ ,  $Sb_2Te_3$ ,  $SiGe$ ,  $(AgSbTe_2)_{1-x}(GeTe)_x$ ,  $PbTe$ ,  $PbSe$ ,  $ZnSb$ , and skutterudites.

79. The system of Claim 78, wherein the  $(AgSbTe_2)_{1-x}(GeTe)_x$  comprises a  $GeTe$  mole fraction of  $\sim 0.80$  to  $0.85$ .

80. The system of Claim 77, wherein said thermoelectric pair in at least one of the at least one upper thermoelectric unit and the at least one lower thermoelectric unit comprises:

at least one of a superlattice and a quantum dot superlattice.

5 81. The system of Claim 80, wherein said superlattice comprises:

at least one of a superlattice of Si/Ge, PbTe/PbSe, ZnSb/CdSb, InAs/InSb, CdTe/HgCdTe,  $Ga_xIn_{1-x}As/Ga_yIn_{1-y}As$ .

82. The system of Claim 77, wherein the at least one upper thermoelectric unit is configured to operate at temperatures from 670K to 870K.

10 83. The system of Claim 77, wherein the at least one lower thermoelectric unit is configured to operate at temperatures from 470K to 670K.

84. The system of Claim 77, wherein the at least one lower thermoelectric unit is configured to operate at temperatures from 300K to 470K.

15 85. The system of Claim 76, wherein said plural cascaded thermoelectric units and said heat sink are configured to have a specific power greater than 1 W/gm.

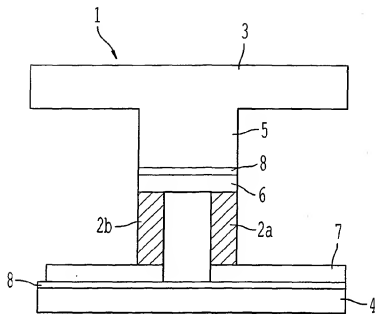
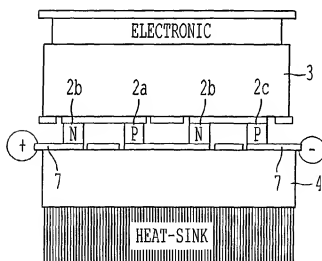
86. The system of Claim 76, wherein said plural cascaded thermoelectric units are configured to have a specific power in a range of 0.0001 W/gm to 0.01 W/gm.

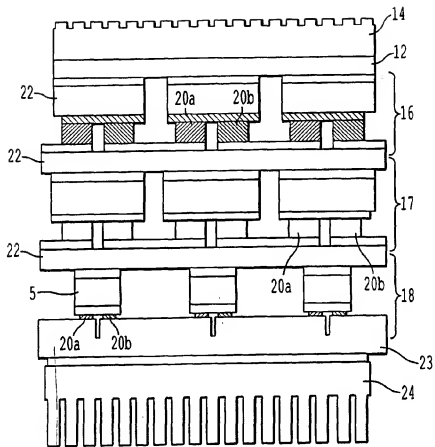
87. The system of Claim 86, wherein the first header is coupled to a heat source in a range of 30-40°C.

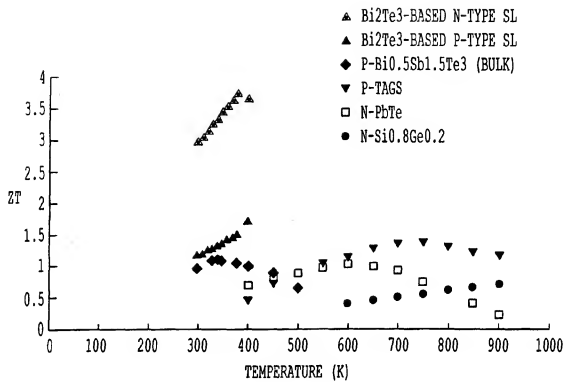
20 88. The system of Claim 76, wherein said plural cascaded thermoelectric units and said heat sink are configured to produce a power density greater than 0.5 W/cm<sup>2</sup>.

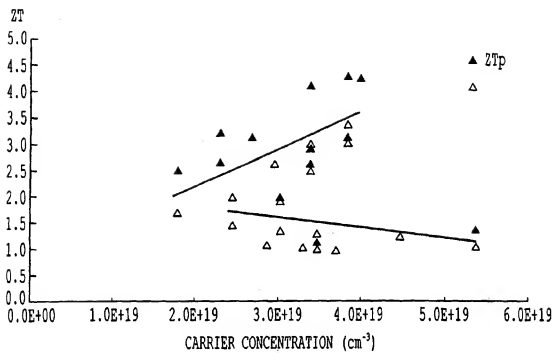
89. The system of Claim 76, wherein said plural cascaded thermoelectric units are configured to produce a power density in a range of 0.0005 W/cm<sup>2</sup> to 0.5 W/cm<sup>2</sup>.

25

*FIG. 1A**FIG. 1B*

*FIG. 2*

*FIG. 3*

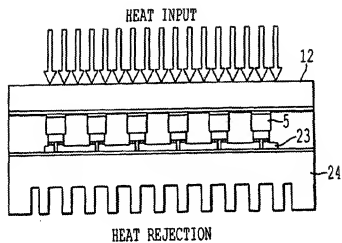
**FIG. 4**



## FIG. 5

TABLE 2

		$T_{\text{heat-sink}} = 300\text{K}$	$T_{\text{heat-sink}} = 323\text{K}$
		$T_{\text{heat-source}} = 845\text{K}$	$T_{\text{heat-source}} = 893\text{K}$
UPPER PROJECTION	$ZT_{\text{ave}}$	EFFICIENCY (%)	EFFICIENCY (%)
Stage 1 (Bi <sub>2</sub> Te <sub>3</sub> -based SL)	2.5	11.4%; OT = 150C	10.8%; OT = 150C
Stage 2 (with PbTe/PbSe SL)	1.5	6.9%; OT = 175C	7.4%; OT = 200C
Stage 3 (with Si/Ge SL)	1.5	5.9%; OT = 200C	5.5%; OT = 200C
Total Efficiency and Power Density for 3-stage Cascade Module		24.2%;	23.7%;
MID-RANGE PROJECTION	$ZT_{\text{ave}}$	EFFICIENCY (%)	EFFICIENCY (%)
Stage 1 (Bi <sub>2</sub> Te <sub>3</sub> -based SL)	2.25	10.8%; OT = 150C	10.2%; OT = 150C
Stage 2 (with PbTe/PbSe SL)	1	5.3%; OT = 175C	5.7%; OT = 200C
Stage 3 (with Si/Ge SL)	1	4.5%; OT = 200C	4.2%; OT = 200C
Total Efficiency and Power Density for 3-stage Cascade Module		20.6%;	20.1%;
LOWER PROJECTION	$ZT_{\text{ave}}$	EFFICIENCY (%)	EFFICIENCY (%)
Stage 1 (Bi <sub>2</sub> Te <sub>3</sub> -based SL)	2	10.2%; OT = 150C	9.6%; OT = 150C
Stage 2 (use only thin-substrate bulk)	0.75	4.3%; OT = 175C	4.7%; OT = 200C
Stage 3 (use only thin-substrate bulk)	0.75	3.7%; OT = 200C	3.4%; OT = 200C
Total Efficiency and Power Density for 3-stage Cascade Module		18.2%;	17.7%;

**FIG. 6A**

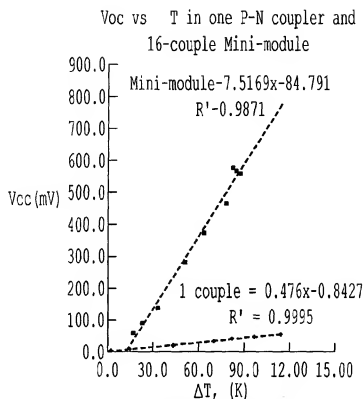


FIG. 6B(1)

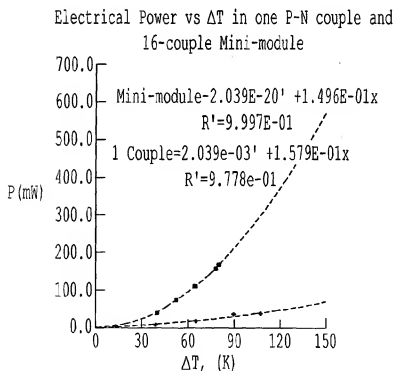
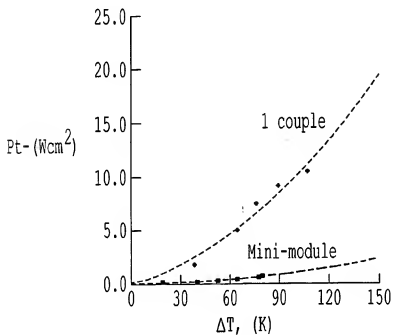


FIG. 6B(2)

Electrical Power Density vs  $\Delta T$  in one P-N couple and  
16-couple Mini-module



*FIG. 6B(3)*

Table 4






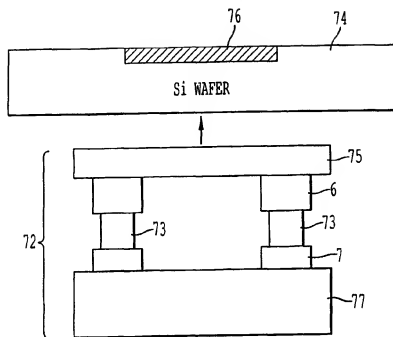
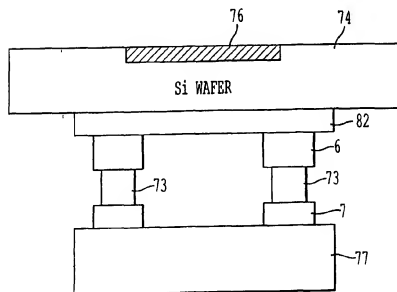
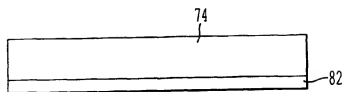
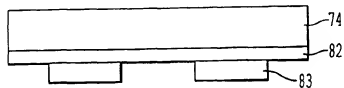
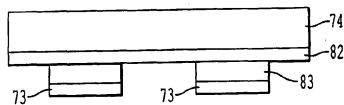
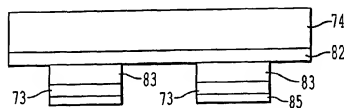
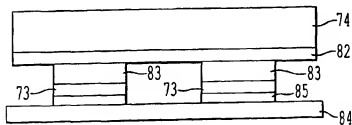
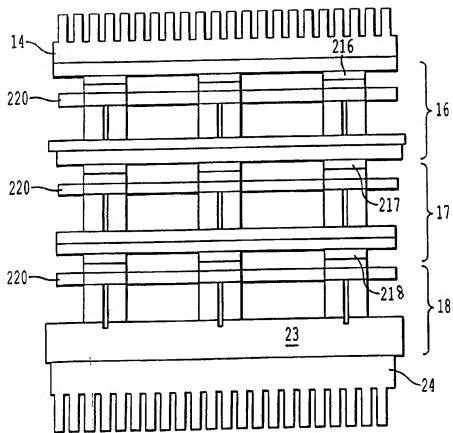
Structure and Comments on Measurement	Configuration	Best Observed ZT	Typical ZT	Potential ZT
P-type Element with two contacts		>3.5	2.5 to 3.0	3.5 to 4.0
N-type Element with two contacts		2.0	1.0 to 1.5	2.0 to 2.5
Invented P-N Couple one interconnect (adiabatic conditions tough but exact thermal-electrical matching between two legs not required to maximize ZT observed)		2.0	1.2 to 1.8	2.0 to 2.5
Mini-module: Flipped; Inverted P-N Couple with one interconnect and two leads on bottom header (adiabatic conditions difficult plus exact thermal-electrical matching between two legs needed to maximize ZT observed by Harman method)		-1.6 (limited by lead resistances on the bottom header)	-1.8 (limited by lead resistances on the bottom header)	>2.0
Mini-module: Flipped, inverted P-N Couple with one interconnect and two leads on bottom header (power mode where ZT is exacted from electrical power and heat flow through SE elements; no need for adiabaticity and thermal matching of legs less stringent (as one leg does not pump on other as in cooling mode when mismatched))		-1.6 (limited by lead resistances on the bottom header)	-1.6 (limited by lead resistances on the bottom header)	>2.0

FIG. 6C

*FIG. 7A**FIG. 7B*

*FIG. 7C(a)**FIG. 7C(b)**FIG. 7C(c)**FIG. 7C(d)**FIG. 7C(e)*



*FIG. 8*



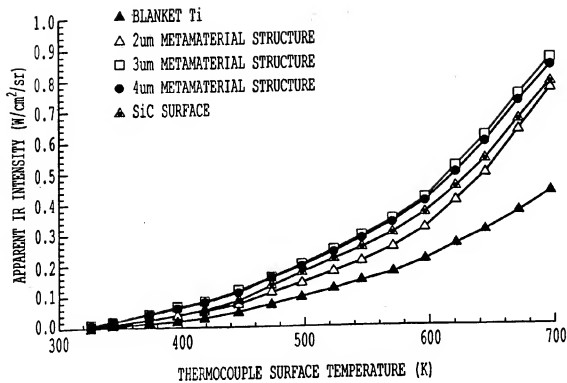
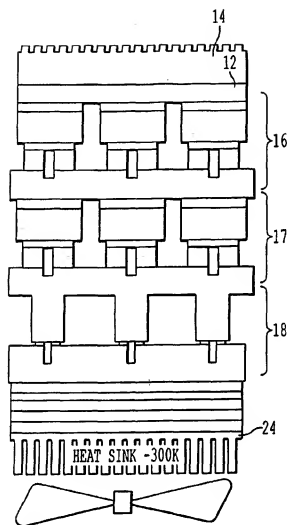


FIG. 9

*FIG. 10*

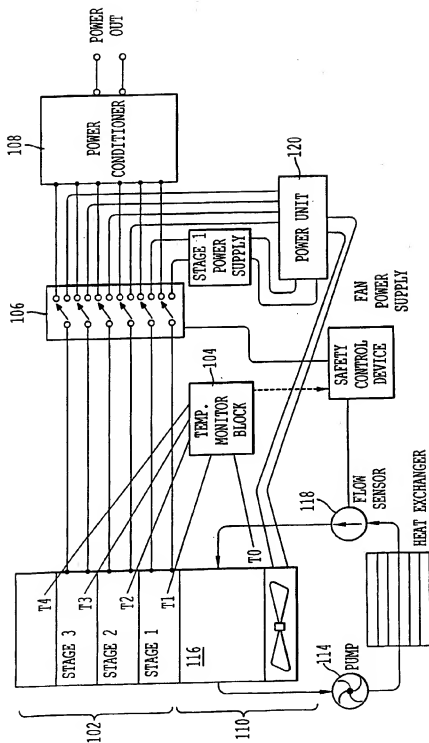
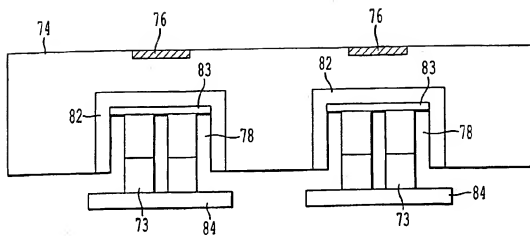
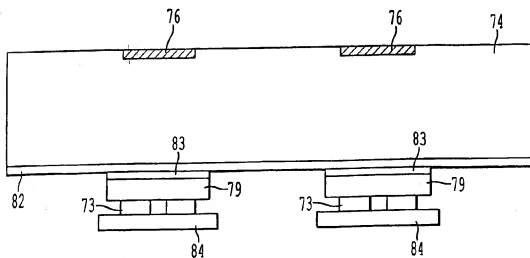
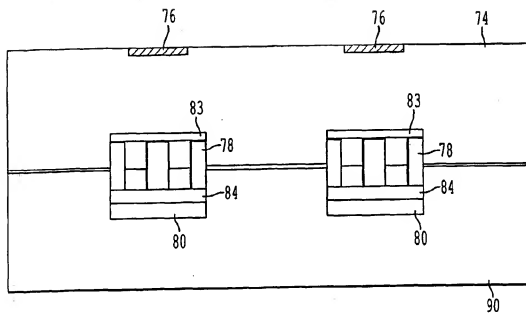


FIG. 11

*FIG. 12A**FIG. 12B*

*FIG. 13*

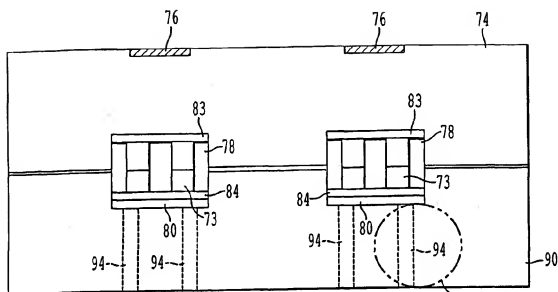


FIG. 14A

FIG. 14B

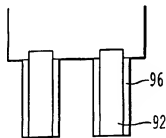
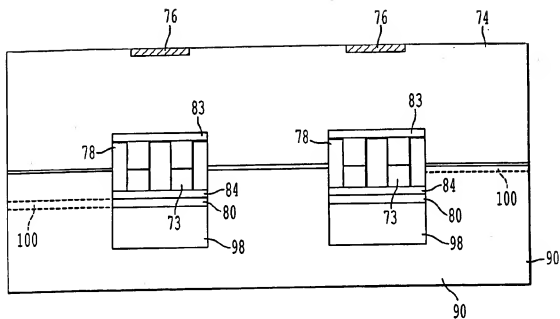


FIG. 14C

*FIG. 15*